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COMMUTATION RULES FOR MATRICES RELATED TO PARTICLES OF HIGHER SPINS

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Introduction

Dirac (1936), Fierz (1939), and Fierz and Pauli (1939) have set up relativistic wave equations for particles with arbitrary spin, and the special cases of spins 3/2 and 2 have been treated in detail in the last of the papers mentioned. For the simpler cases of spins 0 and 1, Kemmer (1939) has given a theory including both types of particles by writing the wave equation in the form*

$$\partial_\mu \beta_\mu \psi + \chi \psi = 0 \tag{1}$$

analogous to Dirac's wave equation of the electron, where the matrices do *not* however satisfy the commutation rules of Dirac matrices, *viz.*,

$$\frac{1}{2}(\beta_\mu \beta_\nu + \beta_\nu \beta_\mu) = \delta_{\mu\nu} \tag{2}$$

but the commutation relation given by Duffin (1938) *viz.*,

$$\beta_\mu \beta_\nu \beta_\rho + \beta_\rho \beta_\nu \beta_\mu = \beta_\mu \delta_{\nu\rho} + \beta_\rho \delta_{\mu\nu}. \tag{3}$$

It is interesting to investigate if a similar theory can be set up for particles of higher spins, in particular 3/2 and 2. The necessary preliminary to this would be the derivation of the commutation rules satisfied by the matrices in these cases. We proceed to show that under suitable assumptions it is possible to derive these commutation rules (see equations 26 and 34).

Method of obtaining commutation rules

(i) The first condition we use is that the equation (1) be relativistic invariant. Under an infinitesimal four-dimensional rotation given by

$$x_\mu' = x_\mu + \epsilon_{\mu\nu} x_\nu, \tag{4}$$

where $\epsilon_{\mu\nu} = -\epsilon_{\nu\mu}$, let the transformation of the ψ be expressed as

$$\psi' = S\psi \tag{5}$$

* The notation used is the same as that of Kemmer's paper, except that we replace the mass term κ by χ.

where $S = 1 + \frac{1}{2}\epsilon_{\mu\nu} t_{\mu\nu}$, and $t_{\mu\nu} = -t_{\nu\mu}$ (6)

The $t_{\mu\nu}$ are square matrices of the same number of rows and columns as the wave function ψ.

As is well known, the wave equation is invariant if

$$\beta_\mu t_{\nu\rho} - t_{\nu\rho}\beta_\mu = \delta_{\mu\nu}\beta_\rho - \delta_{\mu\rho}\beta_\nu \tag{7}$$

The spin operator $S_{\mu\nu}$ is given by

$$t_{\mu\nu} = iS_{\mu\nu} \tag{8}$$

(ii) We shall next assume that $S_{\mu\nu}$ (or $t_{\mu\nu}$) can be expressed in the form

$$t_{\mu\nu} = k(\beta_\mu \beta_\nu - \beta_\nu \beta_\mu) \tag{9}$$

where k is an arbitrary numerical constant. A justification for this assumption is afforded by the fact that as a consequence of (7) and (9) we can deduce the commutation relations characteristic of all infinitesimal rotations (Pauli, 1933). These last relations can be written using the $t_{\mu\nu}$'s, in the form

$$t_{\lambda\mu} t_{\nu\rho} - t_{\nu\rho} t_{\lambda\mu} = \delta_{\mu\nu} t_{\lambda\rho} + \delta_{\lambda\rho} t_{\mu\nu} - \delta_{\lambda\nu} t_{\mu\rho} - \delta_{\mu\rho} t_{\lambda\nu} \tag{10}$$

and is merely an extension to four dimensions of the well-known exchange relations for three-dimensional spin operators, *viz.*,

$$S_1 S_2 - S_2 S_1 = iS_3, \text{ etc.}$$

The left-hand member can be written, using (9), and the notation of Poisson brackets, as

$$\begin{aligned}
&k\{(\beta_\lambda \beta_\mu, t_{\nu\rho}) - (\beta_\mu \beta_\lambda, t_{\nu\rho})\} \\
&= k\{\beta_\lambda (\beta_\mu, t_{\nu\rho}) + (\beta_\lambda, t_{\nu\rho})\beta_\mu - \beta_\mu (\beta_\lambda, t_{\nu\rho}) - (\beta_\mu, t_{\nu\rho})\beta_\lambda\} \\
&= k\{\beta_\lambda (\delta_{\mu\nu}\beta_\rho - \delta_{\mu\rho}\beta_\nu) + (\delta_{\lambda\nu}\beta_\rho - \delta_{\lambda\rho}\beta_\nu)\beta_\mu \\
&\qquad - \beta_\mu (\delta_{\lambda\nu}\beta_\rho - \delta_{\lambda\rho}\beta_\nu) - (\delta_{\mu\nu}\beta_\rho - \delta_{\mu\rho}\beta_\nu)\beta_\lambda\} \\
&= \delta_{\lambda\nu} t_{\lambda\rho} + \delta_{\lambda\rho} t_{\mu\nu} - \delta_{\lambda\nu} t_{\mu\rho} - \delta_{\mu\rho} t_{\lambda\nu}.
\end{aligned}$$

The equations (7) and (9) do not refer to any particular spin value, and eliminating $t_{\mu\nu}$'s between them, we get relations involving only the β_μ's which might be considered as general commutation rules valid for all spins. This elimination is immediate and leads to the result

$$k(\beta_\mu, (\beta_\nu, \beta_\rho)) = \delta_{\mu\nu}\beta_\rho - \delta_{\mu\rho}\beta_\nu. \tag{11}$$

The case $\nu = \rho$ can be excluded since it is trivial, making both sides of (7) identically equal to zero.

(iii) The next equation we use is the algebraic one giving the eigenvalues of the spin operator. Thus we take the eigen-values of any

component of the spin operator $S_{\lambda\mu}$ to be

$-3/2, -1/2, +1/2, +3/2$ for the case of spin 3/2;

$-2, -1, 0, +1, +2$ for the case of spin 2.

Using (8) this gives the algebraic equations

$$t_{\lambda\mu}{}^4+\frac{5}{2}\,t_{\lambda\mu}{}^2+\frac{9}{16}=0 \qquad \text{for spin } \frac{3}{2}; \qquad (12, a)$$

$$t_{\lambda\mu}{}^5+5\,t_{\lambda\mu}{}^3+4\,t_{\lambda\mu}=0 \qquad \text{for spin 2.} \qquad (12, b)$$

The commutation rules can be derived with the help of (11) and (12).

Before proceeding further, we can introduce a little simplification in the work by getting rid of the arbitrary constant k in (9) by making the substitution

$$\sqrt{k}\;\beta_\mu=\beta_\mu'. \qquad (13)$$

The transformed equations can now be written (omitting the dashes) as

$$t_{\mu\nu}=(\beta_\mu, \beta_\nu) \qquad (9, a)$$

$$(\beta_\mu, t_{\nu\rho})=(\beta_\mu, (\beta_\nu, \beta_\rho))=\delta_{\mu\nu}\beta_\rho-\delta_{\mu\rho}\beta_\nu \;(\nu\neq\rho) \qquad (11, a)$$

and (12) retains its form. Also (11, *a*) is equivalent to the two equations

$$\left.\begin{aligned} &(\beta_\nu, t_{\nu\rho})=(\beta_\nu, (\beta_\nu, \beta_\rho))=\beta_\rho \\ \textit{i.e.,}\quad &\beta_\rho=\beta_\rho\beta_\nu{}^2-2\,\beta_\nu\beta_\rho\beta_\nu+\beta_\nu{}^2\beta_\rho \end{aligned}\right\}\ \nu\neq\rho \qquad (14)$$

$$\left.\begin{aligned} &\text{and}\quad (\beta_\mu, t_{\nu\rho})=(\beta_\mu, (\beta_\nu, \beta_\rho))=0 \\ &\text{also}\quad (\beta_\nu, t_{\mu\rho})=(\beta_\nu, (\beta_\mu, \beta_\rho))=0 \\ &\text{or}\quad \beta_\mu\beta_\nu\beta_\rho+\beta_\rho\beta_\nu\beta_\mu=\beta_\nu\beta_\rho\beta_\mu+\beta_\mu\beta_\rho\beta_\nu=\beta_\rho\beta_\mu\beta_\nu+\beta_\nu\beta_\mu\beta_\rho=0 \end{aligned}\right\}\ \mu\neq\nu\neq\rho \qquad (15)$$

In virtue of (15), the 24 products of the type $\beta_\mu\beta_\nu\beta_\rho$ $(\mu\neq\nu\neq\rho)$ formed out of the β's can be grouped into four independent expressions of the form $\beta_\mu\beta_\nu\beta_\rho+\beta_\rho\beta_\nu\beta_\mu$, and we write $\beta_\mu\beta_\nu\beta_\rho+\beta_\rho\beta_\nu\beta_\mu=\gamma_\lambda$ $(\lambda=1, 2, 3, 4)$ (16)

where λ, μ, ν, ρ are all different.

We shall also have frequent occasion to use the following identities relating to Poisson brackets.

$$\left.\begin{aligned} &(xy, z)=x\,(y, z)+(x, z)\,y \\ &(x^n, y)=x^{n-1}\,(x, y)+x^{n-2}\,(x, y)\,x+\cdots+x\,(x, y)\,x^{n-2}+(x, y)\,x^{n-1} \end{aligned}\right\} \qquad (17)$$

where n is a positive integer. The second one is easily deduced by successive applications of the first identity.

Case of spin 3/2

The commutation rules consist in the expression of groups of terms which are products of the β's of the fourth degree in terms of those of lower degree. We therefore require the use of four indices which we denote by λ, μ, ν, ρ. Five cases arise according as the indices are repeated or not as follows:—

(*a*) All the indices equal,

(*b*) Three indices equal, and the fourth different,

(*c*) Two indices equal, and the remaining two also equal,

(*d*) Two indices equal, and the remaining two different,

(*e*) All four indices different.

We now take the Poisson bracket of both sides of the equation (12 *a*) with β_μ. This gives

$$(t_{\lambda\mu}{}^4, \beta_\mu) + \frac{5}{2}(t_{\lambda\mu}{}^2, \beta_\mu) = 0$$

which can be simplified by using (17) and (14). Taking the Poisson bracket (which we shall hereafter denote by P.B. for brevity) with β_μ successively three more times in this manner we get, after some tedious calculation,

$$\beta_\lambda{}^4 - \frac{5}{2}\beta_\lambda{}^2 + \frac{9}{16} = 0 \tag{18}$$

which is the commutation rule for case (*a*).

Next take the P.B. of (18) with $t_{\lambda\mu}$. This gives

$$(\beta_\lambda{}^4, t_{\lambda\mu}) = \frac{5}{2}(\beta_\lambda{}^2, t_{\lambda\mu}), \text{ and using (17) and (14)}$$

$$\beta_\lambda{}^3\beta_\mu + \beta_\lambda{}^2\beta_\mu\beta_\lambda + \beta_\lambda\beta_\mu\beta_\lambda{}^2 + \beta_\mu\beta_\lambda{}^3 = \frac{5}{2}(\beta_\lambda\beta_\mu + \beta_\mu\beta_\lambda). \tag{19}$$

From (14), $\beta_\mu = \beta_\mu\beta_\lambda{}^2 - 2\beta_\lambda\beta_\mu\beta_\lambda + \beta_\lambda{}^2\beta_\mu$

and hence, $\beta_\lambda\beta_\mu = \beta_\lambda\beta_\mu\beta_\lambda{}^2 - 2\beta_\lambda{}^2\beta_\mu\beta_\lambda + \beta_\lambda{}^3\beta_\mu$,

$$\beta_\mu\beta_\lambda = \beta_\mu\beta_\lambda{}^3 - 2\beta_\lambda\beta_\mu\beta_\lambda{}^2 + \beta_\lambda{}^2\beta_\mu\beta_\lambda.$$

These two relations, in combination with (19), give

$$\left.\begin{aligned} 4(\beta_\lambda{}^3\beta_\mu + \beta_\mu\beta_\lambda{}^3) &= 7(\beta_\lambda\beta_\mu + \beta_\mu\beta_\lambda) \\ 4(\beta_\lambda{}^2\beta_\mu\beta_\lambda + \beta_\lambda\beta_\mu\beta_\lambda{}^2) &= 3(\beta_\lambda\beta_\mu + \beta_\mu\beta_\lambda) \end{aligned}\right\} \tag{20}$$

which are the commutation relations for the case (*b*).

Next, taking the P.B. of (20) with $t_{\lambda\mu}$, and using (18) we get

$$\left.\begin{aligned} 4(\beta_\lambda{}^2\beta_\mu{}^2+2\beta_\mu\beta_\lambda{}^2\beta_\mu+\beta_\mu{}^2\beta_\lambda{}^2)+4(\beta_\lambda\beta_\mu\beta_\lambda\beta_\mu+\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda)&=6\beta_\lambda{}^2+14\beta_\mu{}^2-\frac{9}{2}\\ 4(\beta_\mu{}^2\beta_\lambda{}^2+2\beta_\lambda\beta_\mu{}^2\beta_\lambda+\beta_\lambda{}^2\beta_\mu{}^2)+4(\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda+\beta_\lambda\beta_\mu\beta_\lambda\beta_\mu)&=6\beta_\mu{}^2+14\beta_\lambda{}^2-\frac{9}{2}\end{aligned}\right\}\quad(21)$$

From the relations (14)

$$\beta_\lambda{}^2=\beta_\lambda\beta_\mu{}^2\beta_\lambda-2\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda+\beta_\mu{}^2\beta_\lambda{}^2=\beta_\lambda{}^2\beta_\mu{}^2-2\beta_\lambda\beta_\mu\beta_\lambda\beta_\lambda+\beta_\lambda\beta_\mu{}^2\beta_\lambda$$

i.e.,
$$(\beta_\mu{}^2\beta_\lambda{}^2+2\beta_\lambda\beta_\mu{}^2\beta_\lambda+\beta_\lambda{}^2\beta_\mu{}^2)-2(\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda+\beta_\lambda\beta_\mu\beta_\lambda\beta_\mu)=2\beta_\lambda{}^2$$

Similarly,
$$(\beta_\lambda{}^2\beta_\mu{}^2+2\beta_\mu\beta_\lambda{}^2\beta_\mu+\beta_\mu{}^2\beta_\lambda{}^2)-2(\beta_\lambda\beta_\mu\beta_\lambda\beta_\mu+\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda)=2\beta_\mu{}^2\quad(22)$$

Combining (21) and (22) we get

$$\left.\begin{aligned} 4(\beta_\lambda\beta_\mu\beta_\lambda\beta_\mu+\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda)&=2(\beta_\lambda{}^2+\beta_\mu{}^2)-\frac{3}{2}\\ \beta_\lambda{}^2\beta_\mu{}^2+2\beta_\lambda\beta_\mu{}^2\beta_\lambda+\beta_\mu{}^2\beta_\lambda{}^2&=(3\beta_\lambda{}^2+\beta_\mu{}^2)-\frac{3}{4}\\ \beta_\mu{}^2\beta_\lambda{}^2+2\beta_\mu\beta_\lambda{}^2\beta_\mu+\beta_\lambda{}^2\beta_\mu{}^2&=(3\beta_\mu{}^2+\beta_\lambda{}^2)-\frac{3}{4}\end{aligned}\right\}\quad(23)$$

which are the commutation rules for the case (*c*).

The rules for the cases (*d*) can be obtained either by taking the P.B. of (23) with $t_{\mu\nu}$ or of (20) with $t_{\lambda\nu}$. Taking the P.B. of the first expression of (23) with $t_{\mu\nu}$ we get by using (15), *viz.*, that β_λ commutes with $t_{\mu\nu}$,

$$4(\beta_\lambda\beta_\nu\beta_\lambda\beta_\mu+\beta_\lambda\beta_\mu\beta_\lambda\beta_\nu+\beta_\nu\beta_\lambda\beta_\mu\beta_\lambda+\beta_\mu\beta_\lambda\beta_\nu\beta_\lambda)=2(\beta_\mu\beta_\nu+\beta_\nu\beta_\mu).$$

Using the notation of (16) this can be written as

$$2(\beta_\lambda\gamma_\rho+\gamma_\rho\beta_\lambda)=(\beta_\mu\beta_\nu+\beta_\nu\beta_\mu).\qquad(24,\ a)$$

It can be shown similarly that the second relation of (23) gives the same result as (24 *a*).

Next, taking the P.B. of the second relation of (20) with $t_{\lambda\nu}$, we get

$$4(\beta_\lambda\gamma_\rho+\gamma_\rho\beta_\lambda)+4(\beta_\lambda\beta_\mu\beta_\lambda\beta_\nu+\beta_\nu\beta_\lambda\beta_\mu\beta_\lambda)=3(\beta_\mu\beta_\nu+\beta_\nu\beta_\mu)$$

and in view of (24 *a*), therefore

$$4(\beta_\lambda\beta_\mu\beta_\lambda\beta_\nu+\beta_\nu\beta_\lambda\beta_\mu\beta_\lambda)=(\beta_\mu\beta_\nu+\beta_\nu\beta_\mu).\qquad(24,\ b)$$

The first relation of (20) gives

$$4(\beta_\lambda{}^2\beta_\nu\beta_\mu+\beta_\nu\beta_\lambda{}^2\beta_\mu+\beta_\mu\beta_\lambda{}^2\beta_\nu+\beta_\mu\beta_\nu\beta_\lambda{}^2)+4(\beta_\lambda\beta_\mu\beta_\lambda\beta_\nu+\beta_\nu\beta_\lambda\beta_\mu\beta_\lambda)=7(\beta_\mu\beta_\nu+\beta_\nu\beta_\mu)$$

and using (24 *b*), and interchanging μ and ν,

$$2(\beta_\lambda{}^2\beta_\mu\beta_\nu+\beta_\mu\beta_\lambda{}^2\beta_\nu+\beta_\nu\beta_\lambda{}^2\beta_\mu+\beta_\nu\beta_\mu\beta_\lambda{}^2)=3(\beta_\mu\beta_\nu+\beta_\nu\beta_\mu).\quad(24,\ c)$$

Relations (24) are the commutation rules for the case (*d*).

Finally, we take the P.B. of (24) with $t_{\lambda\rho}$ which commutes with both β_μ and β_ν. Since

$$(\gamma_\rho, t_{\lambda\rho}) = \gamma_\lambda$$

(24 *a*) gives

$$(\beta_\rho \gamma_\rho + \gamma_\rho \beta_\rho) + (\beta_\lambda \gamma_\lambda + \gamma_\lambda \beta_\lambda) = 0 \quad \text{(no summation)}.$$

Similarly (24 *b*) and (24 *c*) both give

$$\beta_\nu \gamma_\nu + \gamma_\nu \beta_\nu = 0 \quad \text{(no summation)}.$$

Hence the commutation rules for case (*e*) are of the form

$$\beta_\lambda \gamma_\lambda + \gamma_\lambda \beta_\lambda = 0 \quad (\lambda = 1, 2, 3, 4), \text{ and with no summation} \qquad (25, a)$$

or, written at length

$$\beta_\lambda (\beta_\mu \beta_\nu \beta_\rho + \beta_\rho \beta_\nu \beta_\mu) + (\beta_\mu \beta_\nu \beta_\rho + \beta_\rho \beta_\nu \beta_\mu) \beta_\lambda = 0$$

or,

$$\beta_\lambda \beta_\mu \beta_\nu \beta_\rho + \beta_\lambda \beta_\rho \beta_\nu \beta_\mu + \beta_\mu \beta_\nu \beta_\rho \beta_\lambda + \beta_\rho \beta_\nu \beta_\mu \beta_\lambda = 0. \qquad (25)$$

Equations (18), (20), (23), (24) and (25) constitute the complete set of commutation rules (along with 11*a*, which holds for all spins) for spin 3/2 and it only remains to combine them and express them in one single rule. It can be easily verified, by suitably adjusting numerical constants, that all the above rules are included in the following:—

$$\begin{aligned} 2\,(\beta_\lambda \beta_\mu \beta_\nu \beta_\rho + \beta_\lambda \beta_\rho \beta_\nu \beta_\mu + \beta_\mu \beta_\nu \beta_\rho \beta_\lambda + \beta_\rho \beta_\nu \beta_\mu \beta_\lambda) \\ = 3\,(\beta_\lambda \beta_\mu + \beta_\mu \beta_\lambda)\,\delta_{\nu\rho} + 3\,(\beta_\lambda \beta_\rho + \beta_\rho \beta_\lambda)\,\delta_{\mu\nu} \\ + (\beta_\nu \beta_\rho + \beta_\rho \beta_\nu)\,\delta_{\lambda\mu} + (\beta_\mu \beta_\nu + \beta_\nu \beta_\mu)\,\delta_{\lambda\rho} \\ + (\beta_\mu \beta_\rho + \beta_\rho \beta_\mu)\,\delta_{\lambda\nu} + (\beta_\lambda \beta_\nu + \beta_\nu \beta_\lambda)\,\delta_{\mu\rho} \\ - \frac{3}{2}\,(\delta_{\lambda\mu}\delta_{\nu\rho} + \delta_{\lambda\nu}\delta_{\mu\rho} + \delta_{\mu\nu}\delta_{\lambda\rho}) \end{aligned} \qquad (26)$$

Case of spin 2

Here we require five indices which we denote by $\lambda, \mu, \nu, \rho, \epsilon$. Since the indices take on values from 1 to 4, they cannot all be equal, and we have the following six cases to consider :—

(*a*) All indices equal,

(*b*) Four indices equal, one different,

(*c*) Three indices equal, remaining two equal,

(*d*) Three indices equal, remaining two different,

(*e*) Two indices equal, two others equal, and the last one different,

(*f*) Two indices equal, remaining all different.

Proceeding as in the case of spin 3/2, we take the P.B. of (12, *b*) with β_μ five times successively, and simplifying with the aid of (17) and (14) we get

$$\beta_\lambda{}^5 - 5\,\beta_\lambda{}^3 + 4\,\beta_\lambda = 0 \qquad \text{[Case } (a)\text{]} \tag{27}$$

Next, taking the P.B. of (27) with $t_{\lambda\mu}$ gives

$$(\beta_\lambda{}^4\beta_\mu + \beta_\mu{}^3\beta_\mu\beta_\lambda + \beta_\lambda{}^2\beta_\mu\beta_\lambda{}^2 + \beta_\lambda\beta_\mu\beta_\lambda{}^3 + \beta_\mu\beta_\lambda{}^4) - 5\,(\beta_\lambda{}^2\beta_\mu + \beta_\lambda\beta_\mu\beta_\lambda + \beta_\mu\beta_\lambda{}^2) + 4\,\beta_\lambda = 0 \tag{28}$$

From (14), $\beta_\mu\beta_\lambda{}^2 = \beta_\mu\beta_\lambda{}^4 - 2\,\beta_\lambda\beta_\mu\beta_\lambda{}^3 + \beta_\lambda{}^2\beta_\mu\beta_\lambda{}^2$

$$\beta_\lambda\beta_\mu\beta_\lambda = \beta_\lambda\beta_\mu\beta_\lambda{}^3 - 2\,\beta_\lambda{}^2\beta_\mu\beta_\lambda{}^2 + \beta_\lambda{}^3\beta_\mu\beta_\lambda$$

$$\beta_\lambda{}^2\beta_\mu = \beta_\lambda{}^2\beta_\mu\beta_\lambda{}^2 - 2\,\beta_\lambda{}^3\beta_\mu\beta_\lambda + \beta_\lambda{}^4\beta_\mu.$$

Combining (28) with these we have the relations

$$\left.\begin{aligned} \beta_\lambda{}^4\beta_\mu + \beta_\mu\beta_\lambda{}^4 &= (\beta_\lambda{}^2\beta_\mu + 6\,\beta_\lambda\beta_\mu\beta_\lambda + \beta_\mu\beta_\lambda{}^2) \\ \beta_\lambda\beta_\mu\beta_\lambda{}^3 + \beta_\lambda{}^3\beta_\mu\beta_\lambda &= 5\,\beta_\lambda\beta_\mu\beta_\lambda \\ \beta_\lambda{}^2\beta_\mu\beta_\lambda{}^2 &= 2\,\beta_\lambda\beta_\mu\beta_\lambda \end{aligned}\right\} \tag{29}$$

which are the commutation rules for the case (*b*).

Taking the P.B. of (29) again with $t_{\lambda\mu}$, and simplifying with the aid of (27) and (14) we get after some calculation, the four relations

$$\left.\begin{aligned} &5\,(\beta_\lambda{}^2\beta_\mu\beta_\lambda\beta_\mu + \beta_\mu\beta_\lambda\beta_\mu\beta_\lambda{}^2 + 2\,\beta_\lambda\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda) \\ &\quad = (6\,\beta_\lambda\beta_\mu{}^2 + 8\,\beta_\mu\beta_\lambda\beta_\mu + 6\,\beta_\mu{}^2\beta_\lambda) + 10\beta_\lambda{}^3 - 16\,\beta_\lambda \\ &5\,(\beta_\lambda\beta_\mu\beta_\lambda{}^2\beta_\mu + \beta_\lambda{}^2\beta_\mu\beta_\lambda\beta_\mu + \beta_\mu\beta_\lambda\beta_\mu\beta_\lambda{}^2 + \beta_\mu\beta_\lambda{}^2\beta_\mu\beta_\lambda) \\ &\quad = (11\,\beta_\lambda\beta_\mu{}^2 + 8\,\beta_\mu\beta_\lambda\beta_\mu + 11\,\beta_\mu{}^2\beta_\lambda) + 5\,\beta_\lambda{}^3 - 16\,\beta_\lambda \\ &5\,(\beta_\lambda{}^3\beta_\mu{}^2 + 2\,\beta_\mu\beta_\lambda{}^3\beta_\mu + \beta_\mu{}^2\beta_\lambda{}^3) \\ &\quad = (16\,\beta_\mu{}^2\beta_\lambda + 18\,\beta_\mu\beta_\lambda\beta_\mu + 16\,\beta_\lambda\beta_\mu{}^2) + 5\,\beta_\lambda{}^3 - 16\,\beta_\lambda \\ &5\,(\beta_\lambda{}^3\beta_\mu{}^2 + 3\,\beta_\lambda{}^2\beta_\mu{}^2\beta_\lambda + \beta_\lambda\beta_\mu{}^2\beta_\lambda{}^2 + \beta_\mu{}^2\beta_\lambda{}^3) \\ &\quad = (12\,\beta_\lambda\beta_\mu{}^2 + 16\,\beta_\mu\beta_\lambda\beta_\mu + 12\,\beta_\mu{}^2\beta_\lambda) + 40\,\beta_\lambda{}^3 - 32\,\beta_\lambda \end{aligned}\right\} \tag{30}$$

which are the commutation rules for the case (*c*).

To derive the rules for case (*d*) we take the P.B. of (29) with $t_{\lambda\nu}$ and use (14) and (15). Similar results are also obtained when we consider (29) expressed in terms of β_λ and β_ν and then take the P.B. with $t_{\lambda\mu}$. Rules of this kind are given by the following typical ones:—

$$\left.\begin{aligned} \beta_\lambda{}^2\beta_\mu\beta_\lambda\beta_\nu + \beta_\lambda\beta_\mu\beta_\lambda\beta_\nu\beta_\lambda + \beta_\lambda\beta_\nu\beta_\lambda\beta_\mu\beta_\lambda + \beta_\nu\beta_\lambda\beta_\mu\beta_\lambda{}^2 &= 2\gamma_\rho \\ \beta_\lambda{}^2\beta_\mu\beta_\lambda\beta_\nu + \beta_\lambda\beta_\mu\beta_\lambda{}^2\beta_\nu + \beta_\nu\beta_\lambda{}^2\beta_\mu\beta_\lambda + \beta_\nu\beta_\lambda\beta_\mu\beta_\lambda{}^2 &= 3\gamma_\rho \\ \beta_\lambda\,(\beta_\lambda\gamma_\rho + \gamma_\rho\beta_\lambda) + (\beta_\lambda\gamma_\rho + \gamma_\rho\beta_\lambda)\,\beta_\lambda &= 4\gamma_\rho \\ \beta_\lambda{}^3\beta_\mu\beta_\nu + \beta_\mu\beta_\lambda{}^3\beta_\nu + \beta_\nu\beta_\lambda{}^3\beta_\mu + \beta_\nu\beta_\mu\beta_\lambda{}^3 &= 5\gamma_\rho \end{aligned}\right\}. \tag{31}$$

Next to obtain rules for case (*e*), we take the P.B. of (30) with $t_{\lambda\nu}$, or the P.B. of the relations obtained from (30) by interchanging λ and μ with $t_{\mu\nu}$. Making use of (14) and (15) rules of this type depend on

$$\left.\begin{aligned}
&15\,\{\beta_\lambda(\beta_\mu\gamma_\rho+\gamma_\rho\beta_\mu)+(\beta_\mu\gamma_\rho+\gamma_\rho\beta_\mu)\beta_\lambda\}=2(11\,\beta_\lambda{}^2\beta_\nu+8\,\beta_\lambda\beta_\nu\beta_\lambda+11\,\beta_\nu\beta_\lambda{}^2)\\
&\qquad+10(\beta_\mu{}^2\beta_\nu+\beta_\mu\beta_\nu\beta_\mu+\beta_\nu\beta_\mu{}^2)-32\,\beta_\nu\\
&15\,\{\beta_\nu\beta_\lambda\beta_\mu\beta_\lambda\beta_\mu+\beta_\nu\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda+\beta_\lambda\beta_\mu\beta_\lambda\beta_\mu\beta_\nu+\beta_\mu\beta_\lambda\beta_\mu\beta_\lambda\beta_\nu\}\\
&\qquad=2(4\,\beta_\lambda{}^2\beta_\nu+7\,\beta_\lambda\beta_\nu\beta_\lambda+4\,\beta_\nu\beta_\lambda{}^2)+2(\beta_\mu{}^2\beta_\nu+\beta_\mu\beta_\nu\beta_\mu+\beta_\nu\beta_\mu{}^2)-16\,\beta_\nu\\
&15\,\{\beta_\lambda{}^2\beta_\mu\beta_\nu\beta_\mu+\beta_\lambda\beta_\mu\beta_\nu\beta_\mu\beta_\lambda+\beta_\lambda\beta_\mu\beta_\nu\beta_\mu\beta_\lambda+\beta_\mu\beta_\nu\beta_\mu\beta_\lambda{}^2\}\\
&\qquad=(11\,\beta_\lambda{}^2\beta_\nu+8\,\beta_\lambda\beta_\nu\beta_\lambda+11\,\beta_\nu\beta_\lambda{}^2)+5(\beta_\mu{}^2\beta_\nu+\beta_\mu\beta_\nu\beta_\mu+\beta_\nu\beta_\mu{}^2)-16\,\beta_\nu
\end{aligned}\right\}\quad(32)$$

Finally, for the last case we take the P.B. of (31) with $t_{\lambda\rho}$ or of (32) with $t_{\mu\rho}$. These rules are of the types or reducible to

$$\left.\begin{aligned}
&\beta_\lambda(\beta_\rho\gamma_\rho+\gamma_\rho\beta_\rho)+(\beta_\rho\gamma_\rho+\gamma_\rho\beta_\rho)\,\beta_\lambda=\gamma_\lambda\ \text{(no summation)}\\
&\beta_\lambda\beta_\rho\beta_\lambda\beta_\mu\beta_\nu+\beta_\nu\beta_\lambda\beta_\rho\beta_\lambda\beta_\mu+\beta_\mu\beta_\lambda\beta_\rho\beta_\lambda\beta_\nu+\beta_\nu\beta_\mu\beta_\lambda\beta_\rho\beta_\lambda=\gamma_\lambda
\end{aligned}\right\}.\quad(33)$$

We have now to combine the rules (27), (29-33) into a single one. The left-hand side of the first rule in (33) can be derived from the expression

$$(\beta_\lambda\beta_\rho\beta_\epsilon\beta_\mu\beta_\nu+\beta_\lambda\beta_\rho\beta_\nu\beta_\mu\beta_\epsilon+\beta_\lambda\beta_\nu\beta_\mu\beta_\epsilon\beta_\rho+\beta_\lambda\beta_\epsilon\beta_\mu\beta_\lambda\beta_\rho+$$

terms with order of factors reversed), by putting $\epsilon=\lambda$. This suggests the form of the left-hand side of the desired commutation rule. We can show, by properly adjusting the constants, that all the rules are contained in the following:—

$$\begin{aligned}
&3\,(\beta_\lambda\beta_\mu\beta_\nu\beta_\rho\beta_\epsilon+\beta_\lambda\beta_\mu\beta_\epsilon\beta_\rho\beta_\mu+\beta_\lambda\beta_\epsilon\beta_\rho\beta_\nu\beta_\mu+\beta_\lambda\beta_\nu\beta_\rho\beta_\epsilon\beta_\mu\\
&+\beta_\epsilon\beta_\rho\beta_\nu\beta_\mu\beta_\lambda+\beta_\nu\beta_\rho\beta_\epsilon\beta_\mu\beta_\lambda+\beta_\mu\beta_\nu\beta_\rho\beta_\epsilon\beta_\lambda+\beta_\mu\beta_\epsilon\beta_\rho\beta_\nu\beta_\lambda)\\
&=4\,(\mathrm{S}\,\beta_\lambda\beta_\mu\beta_\nu)\,\delta_{\rho\epsilon}+2\,(\mathrm{S}\,\beta_\lambda\beta_\mu\beta_\rho)\,\delta_{\nu\epsilon}+2\,(\mathrm{S}\,\beta_\lambda\beta_\nu\beta_\rho)\,\delta_{\mu\epsilon}\\
&\quad+(\mathrm{S}\,\beta_\mu\beta_\nu\beta_\rho)\,\delta_{\lambda\epsilon}+(\mathrm{S}\,\beta_\mu\beta_\nu\beta_\epsilon)\,\delta_{\lambda\rho}+(\mathrm{S}\,\beta_\mu\beta_\rho\beta_\epsilon)\,\delta_{\lambda\nu}+(\mathrm{S}\,\beta_\nu\beta_\rho\beta_\epsilon)\,\delta_{\lambda\mu}\\
&\quad+2\,(\mathrm{S}\,\beta_\lambda\beta_\rho\beta_\epsilon)\,\delta_{\mu\nu}+2\,(\mathrm{S}\,\beta_\lambda\beta_\nu\beta_\epsilon)\,\delta_{\mu\rho}+4\,(\mathrm{S}\,\beta_\lambda\beta_\mu\beta_\epsilon)\,\delta_{\nu\rho}\\
&\quad-\beta_\lambda(6\,\delta_{\mu\nu}\delta_{\rho\epsilon}+8\,\delta_{\mu\rho}\delta_{\nu\epsilon}+6\,\delta_{\nu\rho}\delta_{\mu\epsilon})-\beta_\mu(7\,\delta_{\lambda\nu}\delta_{\rho\epsilon}+6\,\delta_{\lambda\rho}\delta_{\nu\epsilon}+7\,\delta_{\rho\nu}\delta_{\lambda\epsilon})\\
&\quad-\beta_\nu(7\,\delta_{\lambda\mu}\delta_{\rho\epsilon}+6\,\delta_{\mu\epsilon}\delta_{\lambda\rho}+6\,\delta_{\mu\rho}\delta_{\lambda\epsilon})-\beta_\rho(6\,\delta_{\lambda\mu}\delta_{\nu\epsilon}+6\,\delta_{\lambda\nu}\delta_{\mu\epsilon}+6\,\delta_{\mu\nu}\delta_{\lambda\epsilon})\\
&\qquad-\beta_\epsilon(7\,\delta_{\lambda\mu}\delta_{\nu\rho}+6\,\delta_{\lambda\nu}\delta_{\mu\rho}+6\,\delta_{\mu\nu}\delta_{\lambda\rho}).
\end{aligned}\quad(34)$$

Here, $(\mathrm{S}\,\beta_\mu\beta_\nu\beta_\rho)$ stands for the sum of the six terms obtained by permuting the factors; thus

$$(\mathrm{S}\,\beta_\lambda\beta_\mu\beta_\nu)=(\beta_\lambda\beta_\mu\beta_\nu+\beta_\nu\beta_\mu\beta_\lambda)+(\beta_\mu\beta_\nu\beta_\lambda+\beta_\lambda\beta_\nu\beta_\mu)+(\beta_\nu\beta_\lambda\beta_\mu+\beta_\mu\beta_\lambda\beta_\nu)\quad(35)$$

where the indices need not all be unequal.

In the left-hand side of (34) the first four terms are in the form of the left-hand side of the commutation rule for spin 3/2 multiplied on the left by β_λ. The last four terms are obtained by inverting the order of factors of the first four terms.

Conclusion

The method of derivation of the commutaion rules for spins 3/2 and 2 sketched above is obviously applicable to the case of general spin although the labour of writing down the rules would be very great as we go to higher and higher spins. It is to be noted that the commutation relations (26) and (34) involve the arbitrary constant k introduced in (9), and the relations have to be modified by replacing β_μ by $\sqrt{k}\,\beta_\mu$ in both (26) and (34). As a consequence, in (26), the left-hand side is multiplied by k^2, and all the terms on the right-hand side involving β's by k. Similarly, in (34), the left-hand side is multiplied by k^2, and the terms involving S on the right-hand side by k, the remaining terms being unaffected.

The question of the determination of this arbitrary constant k, the further development of the theory on the basis of the commutation rules, and the connections of the present formalism with that of Fierz and Pauli will be dealt with in a later paper.

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ISOLATION OF HIBISCITRIN FROM THE FLOWERS OF *HIBISCUS SABDARIFFA*: CONSTITUTION OF HIBISCETIN

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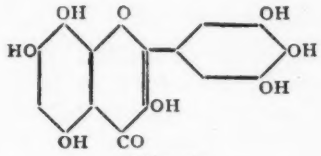
Hibiscus sabdariffa like the *cannabinus*, is a small plant which grows to a height of about three feet. It is largely cultivated all over India as a food plant and also for the sake of its valuable fibre. The stem, branches, ribs and the calyces are red in colour, while the flower petals are pale yellow. But when once the flowers are plucked from the plant, the petals rapidly acquire a red colour. The petals of the *cannabinus*, on the other hand, do not exhibit this characteristic property, and hence it offers a method of distinguishing between the materials obtained from these closely allied species.

The flowers of *H. sabdariffa* were originally examined by Perkin[1] who employed the entire flowers consisting of the stalk, epicalyx, calyx and corolla. He isolated gossypetin and a new yellow compound named "Hibiscetin" as the result of hydrolysis and subsequent ether extraction of the aqueous extract. Regarding the new substance which was obtained in a small yield the data recorded were its melting point and that of its acetyl derivative and no analytical or other details were given. Following the examination of the flowers of *H. cannabinus*,[2] the study of the flowers of the *sabdariffa* has now been taken up in order to compare the closely related species. The general procedure adopted is the same as that described in some of our past publications. When the alcoholic extract is concentrated and allowed to stand, a yellow crystalline solid separates out gradually. It is a new glycoside melting at 238–40° (decomp.). The yellow crystalline aglycone obtained from it by hydrolysis melts at about 350° with decomposition. Since the melting point of the new flavonol and that of its acetyl derivative agree with those given by Perkin for Hibiscetin and its acetyl derivative, it may reasonably be expected that our compound is identical with that of Perkin, and we, therefore, propose to retain the name Hibiscetin. Consequently the glycoside is designated as Hibiscitrin.

Hibiscetin has the formula $C_{15}H_{10}O_9$, undergoes easy decomposition in 50% potash in the cold, and gives a red precipitate with lead acetate. It is, therefore, a hexahydroxy flavonol. On boiling with acetic anhydride and

anhydrous sodium acetate, it produces a heptaacetyl derivative melting at 242–44,° and the latter, when treated with dimethyl sulphate and alkali according to the method of Rao and Seshadri,[4] yields a heptamethyl ether melting at 194–96°. It readily undergoes oxidation with *p*-benzoquinone to give the " gossypetone " reaction, and hence it should contain two hydroxyl groups in 5 and 8 positions. By the decomposition of the heptamethyl ether with boiling 50% potash, trimethyl gallic acid is obtained ; thus the presence of three hydroxyl groups in 3′, 4′ and 5′ positions of the side phenyl nucleus is established. In its colour reactions with buffer solutions and in other properties, the new flavonol resembles gossypetin and occurs along with it in the flowers in the form of the glycosides. Consequently the benzopyrone part of hibiscetin may be expected to be just the same as that of gossypetin, and hence its constitution is given as 3 : 5 : 7 : 8 : 3′ : 4′ : 5′-heptahydroxy flavone.



Hibiscetin

Hibiscetin is, therefore, the more highly hydroxylated member in the herbacetin and gossypetin series. A comparison of the melting points of the three flavonols and their derivatives (see table below) support the above conclusion.

Name	Formula	M.P. of the flavonol	M.P. of the acetyl derivative	M.P. of the methyl ether
Herbacetin	$C_{15}H_{10}O_7$	281–83°	192–93°	157–58°
Gossypetin	$C_{15}H_{10}O_8$	310–12°	228–30°	170–72°
Hibiscetin	$C_{15}H_{10}O_9$	About 350°	242–44°	194–96°

Confirmation of the above constitution of the new flavonol is being sought by synthesis. A complete description of the chemical composition of the flowers will be published later.

Experimental

Isolation of Hibiscitrin.—The dried petals (3 kg.) were extracted with boiling methylated spirits, and the combined alcoholic extract was concentrated to about 800 c.c. After removing the wax and resin that had separated by filtration through fluted filters, the clear concentrate was allowed

to stand. A yellow solid began to appear in about a month, and the deposition seemed to be complete at the end of three months. The solid was filtered and washed well with water till it assumed a lemon-yellow colour. It was, however, not pure, and was sticky to the touch. Therefore a solution of it in a small quantity of pyridine was diluted with water till the impurities began to separate in a colloidal form. They were completely precipitated by the addition of a little calcium chloride, and filtered. On concentrating the clear filtrate to a small bulk a yellow crystalline solid was obtained. One more crystallisation from alcohol rendered the substance pure and it appeared as yellow rectangular plates. On heating, it sintered at about 225°, became a semi-fluid a few degrees higher and decomposed at 238–40°. The yield was 6 g. (Found in the air-dried sample : C, 47·5, H, 4·7; loss on drying at 150° *in vacuo* for 5 hours : 3·0%. $C_{27}H_{30}O_{19}$, H_2O requires C, 47·9, H, 4·7; loss on drying (H_2O), 2·7%. Found in the sample dried at 150° *in vacuo* : C, 48·8, H. 4·2 ; $C_{27}H_{30}O_{19}$ requires C, 49·2, H, 4·6%.)

Preparation of Hibiscetin.—The glycoside (2 g.) was boiled under reflux with 100 c.c. of 7% sulphuric acid. After about 5 minutes the solid completely dissolved forming a clear solution, and another yellow crystalline solid began to separate out within 15 minutes. As there was severe bumping, the boiling had to be carried out over a low flame for the rest of the period (2 hours) to complete the hydrolysis. After cooling, the aglycone was filtered and washed with a little water. It was a deep yellow shining crystalline substance, and was almost pure.

Properties.—It was very sparingly soluble in almost all the organic solvents except pyridine from which it crystallised as glistening rectangular plates melting at about 350° with decomposition. (Found in the air-dried sample : C, 50·8 ; H, 3·8 ; $C_{15}H_{10}O_9$, H_2O requires C, 51·1, H, 3·4%. Found in the specimen dried at 120° *in vacuo*: C, 53·6, H, 3·3 ; $C_{15}H_{10}O_9$ requires C, 53·9; H, 3·0%.) When treated with dilute alkali the substance dissolved immediately producing a red solution which rapidly changed to brown. In alcoholic solution it gave a deep red precipitate with neutral lead acetate, and an olive brown colour with ferric chloride. It dissolved in 50% potash producing a deep red solution which, on being left exposed to air for 24 hours with occasional shaking, became opaque and brown. On acidification, the alkaline solution gave no precipitate.

Colour Changes with Alkaline Buffer Solutions.—With alkaline buffer solutions the flavonol exhibited a beautiful and characteristic display of colours as shown in the table given below, and the colour changes were just similar to those given by gossypetin under the same conditions.

pH	Hibiscetin
8·0	Dissolved slowly to form a pale yellow solution which acquired a violet tinge in about 15 minutes. In half an hour the colour was pale violet. The dissolution was only partial and not complete.
8·6	The dissolution was more rapid, and the initial yellow colour changed to dirty green in 3 minutes, to bluish green in 5 minutes and to pure, though not bright blue within a minute more. The final colour which was stable for about 45 minutes began to fade subsequently and was only half the original intensity after an hour. After 2 hours the solution was almost colourless, and the next day it assumed a pale yellow tinge.
9·2	Same changes as above but more rapid ; Yellow solution → greenish yellow (1 min.) → blue (2 min.). The final colour was stable for about half an hour and began to fade as in the former case. After 24 hours it was pale yellow.
9·8	Same changes as above but more quick. The blue colour appeared even within a minute.
10·4	Quick succession of changes: deep yellow → green (15 sec.) → deep blue (30 sec.) → rapid fading → pale yellow (24 hours).
11·0	Same but more rapid changes, the deep blue being observed even within 15 seconds. Within another half a minute the blue began to fade and became pale bluish green in about 2 minutes. It further faded away rapidly, and became almost colourless after 10 minutes. The next day the solution was pale yellow.
11·6	Same changes as above. The disappearance of the final deep blue (10 seconds) was almost complete in about 5 minutes. The colour after 24 hours was pale yellow.
12·2	Immediately dissolved to produce a green solution, and the initial yellow could not be noticed. On shaking the green changed to blue in a moment. The colour began to fade away even within 15 seconds, and almost completely disappeared in a minute. The next day it was brownish yellow.
12·8	Quick succession of changes:— Green → blue → almost colourless (½ min.) → pale brown (2 min.) → brownish yellow (24 hours).

Gossypetone Reaction with the Flavonol.—On account of the sparing solubility of the flavonol in absolute alcohol, the gossypetone reaction had to be carried out with a solution of the substance in a mixture of alcohol and pyridine. A suspension of it (0·25 g.) in absolute alcohol (20 c.c.) was treated with a few drops of pyridine till a clear solution was obtained, and was then mixed with a solution of *p*-benzoquinone in absolute alcohol (0·1 g. in 20 c.c.). The mixture immediately assumed a dull red colour, and within 5 minutes a chocolate red precipitate began to separate out. After half an hour the solid was filtered and washed with a little more absolute alcohol. It was sparingly soluble in water and alcohol, and did not melt below 350°. (Found: C, 54·0, H, 2·6; $C_{15}H_8O_9$ requires C, 54·2, H, 2·4%.) With dilute alkali it produced a brown red solution which changed to reddish yellow on acidification with hydrochloric acid. When a suspension of the substance in water was treated with sulphur dioxide, the original flavonol was generated.

Acetylation of Hibiscetin : Preparation of Heptaacetyl Derivative.—The substance was acetylated by boiling with acetic anhydride and anhydrous sodium acetate for 4 hours. On crystallisation from glacial acetic acid using a little animal charcoal, the acetyl derivative was obtained as colourless narrow rectangular plates. It became a glassy mass at 234–35° and flowed down into a liquid at 242–44°. Mixed melting points with acetyl cannabiscetin and acetyl gossypetin were depressed. (Found: C, 55·7, H, 3·9; $C_{15}H_3O_2(OCOCH_3)_7$ requires C, 55·4; H, 3·8%.)

Methylation of Hibiscetin : Preparation of the Heptamethyl Ether.—Acetyl hibiscetin (1 g.) was dissolved in acetone (50 c.c.) and treated alternately with dimethyl sulphate (10 c.c.) and 20% sodium hydroxide (10 c.c.) in small quantities. There was a gradual rise in temperature throughout the process, and occasionally the contents had to be cooled. Further quantities of dimethyl sulphate (5 c.c.) and the alkali (5 c.c.) were then added and the medium was finally made definitely alkaline by the gradual addition of more alkali (10 c.c.). After leaving overnight, the mixture was boiled under reflux for an hour, and the solvent was then driven off completely. On diluting the solution and adding acid, a pale brown solid was precipitated. It was treated with a small amount of ether to remove the adhering impurities and was then crystallised from alcohol, when it came out as colourless needles and narrow rectangular plates, melting at 194–96°. (Found: OCH_3, 45·8; $C_{15}H_3O_2(OCH_3)_7$, $2H_2O$ requires OCH_3, 46·4%.)

Alkaline Oxidation of the Heptamethyl Ether : Isolation of Trimethyl Gallic Acid.—Heptamethyl hibiscetin (1 g.) was boiled under reflux with 50% alkali (30 c.c.) for six hours in a silver flask. The decomposition mixture was diluted to about 150 c.c. and the clear alkaline solution was acidified with concentrated hydrochloric acid. On ether-extraction an almost colourless crystalline acid was obtained. It was purified by dissolution in sodium bicarbonate, subsequent reprecipitation with hydrochloric acid and final recrystallisation from dilute alcohol. It was thus obtained as colourless long rectangular plates melting at 168–70°, and was found to be identical with trimethyl gallic acid.

Summary

A new flavonol glycoside has been isolated from the flower petals of *Hibiscus sabdariffa*, and has been named Hibiscitrin. Its aglycone, Hibiscetin is a hexahydroxy flavonol forming a heptaacetyl derivative on acetylation. When decomposed with boiling 50% alkali, its heptamethyl ether produces trimethyl gallic acid, indicating thereby the existence of hydroxyl groups in 3′, 4′ and 5′ positions in hibiscetin. On oxidation with *p*-benzoquinone,

the pigment yields the corresponding quinone, and hence it should contain two hydroxyl groups in positions 5 and 8. It resembles gossypetin in many of its properties especially the colour changes with alkaline buffer solutions, and also occurs along with it in the flowers. It is, therefore, expected that the benzopyrone part of hibiscetin would be just the same as in gossypetin, and hence it is assigned the structure of 3: 5 :7: 8: 3′: 4′: 5′-heptahydroxy-flavone.

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RAMAN EFFECT AND HYDROGEN BONDS

Part II. Mixtures of Aldehydes and Ketones with Acceptor Solvents

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In Part I[1] of this series a study of the mixtures of esters with various acceptor solvents was made and the results discussed. In continuation of the work a few typical ketones and aldehydes have now been employed. The Raman spectra of these substances and their mixtures with phenol, methyl and ethyl alcohols and chloroform have been investigated.

The following is the record of the Raman spectra of the aldehydes and ketones as obtained by us and used as standards for comparison.

(1) *Acetone.*—Purified by slow distillation at 56–58°.

386 (0) 480 (0) 535 (1) 790 (7) 1060 (1) 1225 (1) 1352 (0) 1420 (2) 1440 (4) 1710 (5 *b*) 2838 (0) 2922 (10) 2960 (4) 3005 (2).

(2) *Methyl ethyl ketone.*—Purified by slow distillation at 80°.

260 (0) 410 (2) 594 (2) 760 (6) 954 (1) 1000 (1) 1090 (2) 1160 (0) 1414 (2) 1712 (3 *b*) 2917 (1) 2980 (6 *b*).

Whitelaw[2] has reported 1734 cm.$^{-1}$ as the C=O frequency of this substance. Ganesan and Venkateswaran[3] have given 1729 cm.$^{-1}$ whereas Kohlrausch[4] and co-workers have recorded 1712 cm.$^{-1}$ Our value of the C=O frequency agrees with that of Kohlrausch and this appears to be quite reasonable because it is very close to the C=O frequency of acetone as may be expected.

Acetophenone.—Purified by distillation under reduced pressure.

165 (7 *b*) 365 (2) 470 (0) 590 (1) 619 (3) 725 (5) 764 (0) 946 (1) 1000 (10) 1024 (5) 1076 (4) 1160 (2) 1189 (0) 1264 (6) 1420 (1) 1450 (1) 1596 (10) 1678 (10 *b*) 2923 (2 *b*) 2970 (1) 3066 (8 *b*).

Benzaldehyde.—Purified by distillation under reduced pressure in an atmosphere of nitrogen.

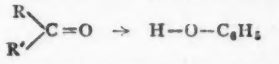
140 (10 *b*) 290 (4 *b*) 440 (6) 610 (6) 650 (2) 825 (4) 1002 (10) 1025 (2) 1164 (10) 1200 (8) 1290 (1) 1456 (1) 1487 (1) 1591 (10) 1698 (10) 3050 (4).

Cinnamic aldehyde.—Distilled under reduced pressure in an atmosphere of nitrogen.

170 (1) 317 (3) 400 (0) 490 (2) 576 (2) 602 (6) 846 (4) 972 (3) 995 (8) 1028 (1) 1068 (2) 1122 (8) 1150 (1) 1180 (7) 1193 (5) 1242 (8) 1300 (2) 1330 (6) 1388 (8) 1450 (2) 1490 (5) 1592 (10) 1624 (10) 1670 (10).

Mixtures with Phenol

Just as in the case of the esters, mixtures of aldehydes and ketones with phenol give prominent effects. Besides the original C=O lines with considerably diminished intensity new lines with smaller frequencies are obtained. The shifts are in general smaller than in the case of the esters. The new lines are attributable to the formation of hydrogen bonds as below :—



where R and R′ are alkyl or aryl groups or hydrogen atoms.

The C=O frequencies in the carbonyl compounds and in the mixtures are embodied in Table I.

TABLE I

Name of the Carbonyl Compound	C=O frequency of the pure substance	C=O frequency of the phenol mixture	Difference
Acetone	1710	1695, 1710	15
Methyl ethyl ketone	1712	1690, 1712	22
Acetophenone	1678	1660, 1678	18
Benzaldehyde	1698	1670, 1698	28
Cinnamic aldehyde	1672	*diffuse	

*The diffuseness in the case of cinnamic aldehyde mixture is towards shorter wavelengths and it definitely indicates that there is a tendency to form molecular associates.

Mixtures with Other Solvents

In regard to the mixtures with other solvents, methyl and ethyl alcohols and chloroform, no noticeable change existed in their spectra as the result of admixture. This is clearly brought out in Table II. There is thus no

TABLE II

Name of the Carbonyl Compound	C=O frequency of the pure substance	C=O frequencies of the mixture		
		With methyl alcohol	With ethyl alcohol	With chloroform
Acetone	1710	1710	1710	1710
Methyl ethyl ketone	1712	1712	1712	1712
Acetophenone	1678	1678	1680	1680
Benzaldehyde	1698	..	..	1696
Cinnamic aldehyde	1670	1670	1670	1670

evidence from the Raman spectra for the formation of hydrogen bonds in these cases.

In regard to the acetone-alcohol mixture it may be recalled here that from a study of the infra-red spectra Go dy[5] reported a shift of the C=O frequency of acetone as a result of admixture with alcohol. However, this observation is not very reliable, as Badger and Bauer[6] have pointed out, because comparison was effected between the observed spectrum of the mixture and that calculated using Beer's law. Adopting the correct procedure, that is by comparison of the spectrum of the mixture with that obtained when the components were placed separately in two absorption cells in series in the absorption path, no difference was noticed by the latter workers. Our observations recorded in the above table support this contention and indicate that the C=O group is not affected.

Discussion

The results reported in this communication offer further support to the conclusions arrived at in Part I and the explanations that were offered. The large variations in the strengths of hydrogen bonds are again noticed in the phenol mixtures obviously depending upon the anionoid power of the donor atoms.

In regard to the other mixtures it is remarkable that no change in the C=O frequencies could be noted. Many examples of this type were reported even in Part I. In these cases it may be taken that the study of the phenomenon through the C=O frequencies indicates no hydrogen bond formation. However, as already stated by us, infra-red data relating to changes in the acceptor part show that hydrogen bond formation is more or less universal in mixtures having donor and acceptor atoms—the types that have been used by us. Thus it becomes necessary to visualise two types of molecular aggregates in one of which the donor group is definitely affected whereas in the other there is no effect on this group. In this connection the proposal of Bernal[7] to classify hydrogen bonds under two types, namely the hydrogen and the hydroxyl bonds may be recalled. The distinction between them lay in a marked difference in the strengths. In the first category called hydrogen bonds the O—H$\cdots$O distance was found to be 2·50–2·65 Å.U. corresponding to an energy of the bond of about 8000 cal./mole. The hydrogen atom was considered to be attached with almost equal firmness to the two oxygen atoms which it joins. This satisfies all the requirements of true hydrogen bonds exhibiting resonance as suggested by Sidgwick.[8] Consequently both the centres, anionoid as well as cationoid, should be affected. In the second category called hydroxyl bonds the O—H$\cdot\cdot$O distance was

found to be 2·7–2·9 Å.U. and the energy involved about 5000 cal./mole. In this bond the hydrogen atom was still regarded as belonging to its parent oxygen and hence it may be expected that the effect on the donor group will be small.

Though the above suggestions of Bernal could be satisfactorily applied for particular cases, owing to practical difficulies in effecting the distinction this classification could not be employed for the large number of cases of hydrogen bonds that have been investigated (mainly by infra-red studies). The criterion adopted by Bernal as feasible for ordinary work utilises the disappearance of the OH band for indicating the existence of hydrogen bonds and its shift towards longer wave-lengths for the hydroxyl bonds. But this has not been found to be satisfactory since later work[9] employing improved methods has revealed the existence of the OH band even in well-established cases of hydrogen bonds in which the band was originally missed. Hence this criterion cannot be employed. Consequently the distinction between the two types of hydrogen bonds has not been widely adopted by workers in this field and both types are referred to only as hydrogen bonds in literature.

The results obtained in the course of the present work indicate the need and also a method for the recognition of two types of hydrogen bonds, (1) the stronger bonds that affect both the anionoid and cationoid centres (*i.e.*, C=O and OH groups) as obtained from Raman and infra-red spectra and (2) the weaker type whose effect is only exhibited in the O–H groups. However, since they are all hydrogen bonds the nomenclature of Bernal does not seem to be quite suitable and hence the following proposal is made for naming them:

(1) True hydrogen bonds;

(2) Hydrogen bonds.

Though there exists large variation in the bond strengths in each group (*vide* Venkateswaran,[10] Murty and Seshadri[1]) the distinction between these two main classes is marked.

With a view to sum up the results obtained with mixtures forming hetero-molecular hydrogen bonds Table III is presented here. The notation employed is as follows:—

(*a*) shift of the C=O frequency. Shifts in cm.$^{-1}$ are given as a_{20} etc.;

(*b*) the appearance of a new line with a shorter frequency. The frequency differences are given as b_{20} etc.;

(*c*) diffuseness of the frequency towards shorter wave-lengths (< 15 wave numbers);

(*d*) no change in the C=O frequency.

TABLE III

Name of the Carbonyl Compound	C=O frequency of the pure substance	Effect of admixture			
		With phenol	With methyl alcohol	With ethyl alcohol	With, chloro-form
1. Ethyl acetate	1739	b_{39}	*c*	*c*	*d*
2. Ethyl benzoate ..	1720	b_{25}	*d*	*d*	*d*
3. Ethyl cinnamate ..	1712	b_{27}	*d*	*d*	*c*
4. Phenyl acetate	1766	b_{50}	b_{20}	b_{20}	b_{20}
5. Phenyl propionate ..	1760	b_{50}	..	..	..
6. Phenyl benzoate ..	1740	b_{36}	..	..	*c*
7. Benzylacetate	1745	b_{30}	..	..	*d*
8. Coumarin	1742	a_{32}	a_{15}	a_{22}	a_{22}
9. Acetone	1710	b_{32}	*d*	*d*	*d*
10. Methyl ethyl ketone ..	1712	b_{22}	..	..	*d*
11. Acetophenone	1678	b_{18}	*d*	*d*	*d*
12. Benzaldehyde	1745	b_{28}	..	..	*d*
13. Cinnamic aldehyde ..	1672	..	*d*	*d*	*d*

From the above table the following points regarding the influence of constitutive factors on the strengths of hydrogen bonds may be noted:—

(*a*) Esters in general form stronger hydrogen bonds than ketones.

(*b*) Phenyl esters as a rule produce stronger bonds than the corresponding alkyl esters.

(*c*) Esters of aliphatic acids give rise to stronger hydrogen bonds than the corresponding esters of aromatic acids.

(*d*) Benzyl esters are similar to the corresponding alkyl esters in this respect.

(*e*) Aliphatic ketones form stronger bonds than aromatic ketones.

(*f*) The conjugation of a C=C with the C=O reduces the hydrogen bond forming capacity as in cinnamates and cinnamic aldehyde.

(*g*) Coumarin forms strong hydrogen bonds and resembles the phenyl esters in this respect. Further, the original C=O frequency completely disappears thus indicating that the association is almost complete.

The abovementioned influences of the constitutive factors on the hydrogen bonds could be readily understood from their effect on the C=O frequency of the compounds concerned. The C=O frequency of esters is higher than that of ketones indicating, thereby, that their C=O bond is stronger and that the group is more powerful as an anionoid centre. The

effect of the phenyl group varies with its location. When it is attached to the 'C' of the C=O through an oxygen atom, as found in phenyl esters, it enhances the C=O frequency and enables it to form stronger hydrogen bonds. If the phenyl group, however, is attached directly to the 'C' of the C=O, as in the case of esters of aromatic acids and in aromatic ketones, the C=O frequencies are lowered and the hydrogen bonds that are formed become weaker. When the phenyl group is separated from the C=O by means of a CH_2 group, as found in the benzyl esters the influence of this group is lost and hence the benzyl esters behave like the alkyl esters. Greater details regarding the influence of constitutive factors on the C=O group have been given in our previous publications.[11]

Summary

The Raman spectra of a few typical aldehydes and ketones and their mixtures with acceptor solvents such as phenol, methyl and ethyl alcohols and chloroform are recorded and the results are discussed. They support the general conclusion arrived at in Part I that large variations in hydrogen bond strengths exist and that they depend upon two factors (1) the anionoid power of the donor atom and (2) the cationoid power of the acceptor atom. The question of distinguishing between two types of hydrogen bonds, the hydrogen and hydroxyl bonds, as suggested by Bernal is discussed in the light of our results. It is shown that there is justification for division into two categories and a proposal is made to effect the classification as below:

(1) True Hydrogen Bonds. (2) Hydrogen Bonds.

In Class (1) both the cationoid (C=O) and anionoid (OH) centres are affected whereas in class (2) only the cationoid group indicates change.

The influences of constitutive factors on the capacity of the carbonyl compounds to form hydrogen bonds are explained as due to their effect on the strength of the C=O group. Similar explanation has already been given in Part I regarding the behaviour of the solvents containing cationoid atom (H atom) in hydrogen bond formation.

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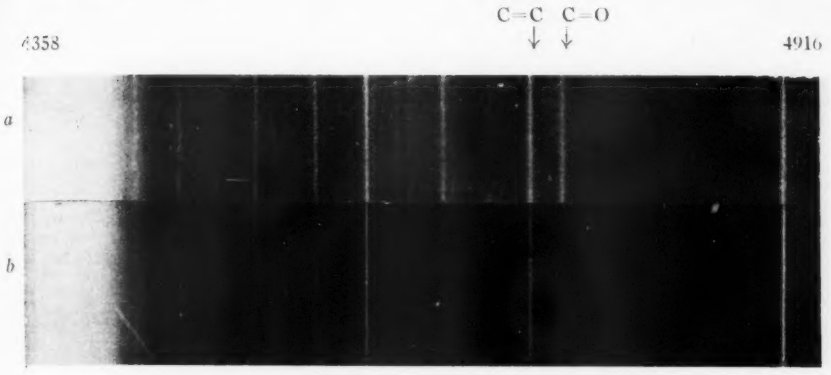
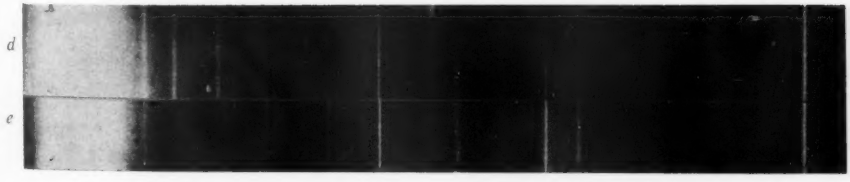
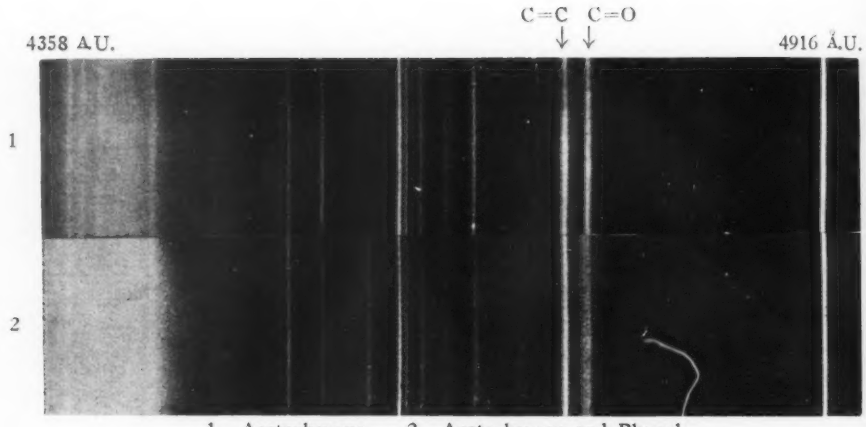


(*a*) Ethyl benzoate. (*b*) Ethyl benzoate in phenol.

(*c*) Phenol.



(*d*) Ethyl benzoate in carbon tetrachloride. (*e*) Ethyl benzoate.



1. Acetophenone. 2. Acetophenone and Phenol.

FATTY ACIDS OF NEEM OIL

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In studying the chemical composition of Neem oil the substances responsible for the following three important properties demand attention: (1) The oil has an obnoxious odour and this seems to be due to a mixture of volatile compounds some of which contain sulphur. (2) It is highly and disagreeably bitter. In a paper by Murti, Rangaswamy and Seshadri[1] the nature of the bitter principles was discussed and the isolation and properties of two bitter substances described. They are not glycosides and have compositions represented by the empirical formulæ $C_5H_7O_2$ and $C_4H_7O_2$. When tested on earthworms and fish they are not found to possess marked toxic properties. (3) The oil is reputed to be an antiseptic and has been used as an anthelmintic and in the treatment of certain skin diseases. The position is not definite regarding the chemical components to which the oil owes these properties. For this purpose too, the volatile portion is probably the most useful. In view of the fact that in certain medicinal oils, such as the chaulmoogra oil, the fatty acids are responsible for the therapeutic action, the fatty acid composition of the Neem oil has also received considerable attention. In this paper a critical examination of the fatty acid components is made.

The results of a large number of workers who studied the fatty acid composition of the Neem oil are in general agreement and the most important of them are presented in Table I. The chief fatty acids are palmitic, stearic, oleic and linoleic acids. Within limits of experimental error they account for the entire composition of the oil. The claim of Chatterjee and Sen[2] to have obtained a special acid called margosic acid may be mentioned here. It was considered to occur to the extent of 24% of the oil and to be responsible for the medicinal properties. But this was disproved by Watson and co-workers[3] and subsequently by Roy and Dutt[4] and Child and Ramanathan.[5] The so-called margosic acid was shown to be a mixture of other known fatty acids. In spite of all previous work recently Qudrat-i-Khuda, Ghosh and Mukherjee[6] have put forward a claim for having isolated four new acids whose glycerides are said to form the main bulk of the oil. Two

TABLE I

	Roy and Dutt[4]	Child and Ramanathan[5]	Hilditch and Murthi[10]	Khuda and others[6]	Present sample
Sp. gr.	0·9162 at 10·5° C.	0·9159	..	0·9108 at 22·9° C.	0·9129 at 31° C.
Ref. Index	..	1·4620	..	1·46185 at 22·9° C.	1·4658 at 31° C.
Sap. Val.	197·0	201·0	197·0	198·8	195·6
Iod. Val.	74·3	71·5	67·9	69·56	69·2
Unsap.	1·2	0·7	1·7	..	1·9
Acid value	9·5	..	18·0	..	11·2
Sat. Acids					
Lower fatty acids ..	2·3	..	..	..	..
Palmitic	12·62	13·1	14·9	Acids	13·8
Stearic	21·38	18·5	14·4	A and B	18·2
Arachidic	0·74	2·3	1·3		1·8
Unsat. Acids					
Oleic	52·08	47·5	61·9	Acids	52·6
Linoleic	2·12	15·13	7·5	C and D	13·6

of these, A and B are saturated and the other two, C and D unsaturated. Their properties are presented in Table II.

TABLE II

	M.P.	M.Wt.	Carbon %	Hydrogen %	Formulæ
Acid A	67° C. ..	232·4	74·21	12·02	$C_{14}H_{28}O_2$ *iso*-tetradecoic
Acid B	55° ..	256·7	75·3	12·2	$C_{16}H_{32}O_2$ *iso*-palmitic
Acid C	47–48° ..	..	75·2	11·57	$C_{15}H_{28}O_2$ Oleic acid series
Acid D	31–33° ..	..	77·01	11·7	$C_{18}H_{32}O_2$ Cyclic series

Though the methods employed by these authors are not accepted standard ones and the characterisation of the acids is not satisfactory, still in view of the importance of the results and the possibility of explaining the important properties of the oil if the presence of any special acids could be proved, their work has been critically examined and repeated as far as possible. From the physical properties and the chemical contents reported by them (see Table I) it can be inferred that they were dealing with a genuine sample of Neem oil. Since none of the previous workers have detected any abnormal acids and they do not obviously seem to have missed any component and Qudrat-i-Khuda *et al.* find the oil to consist entirely of new acids and do not record the presence of any of the ordinary acids, it

becomes necessary to examine how far the proofs are convincing. C_{16} solid acid (B) according to them melts lower than the C_{14} acid (A). Acid C seems to be rather unusual having an odd number of carbon atoms. Acid D said to belong to the cyclic series may be expected to exhibit optical activity and such support is lacking. It is to be noted that though C and D are unsaturated they are solids melting at 47–48° C. and 31–33° C. No support is given for the composition of the acids by the determination of Iodine value or neutralisation value. With reference to the claims for the isolation of acids with 14 and 15 carbon atoms may be mentioned the conclusions of Child and Ramanathan that no acid above C_{20} group and below C_{16} group exist in the oil.

With a view to exhaust all possibilities we have secured a genuine sample of Neem oil from the Ramnad District. Its physical and chemical constants (Table I) were quite normal. Following the method of Khuda *et al.* it was subjected to steam distillation and extraction with water and finally saponified. The total fatty acids were separated into two fractions by filtration under suction. Subsequently by crystallising the solid portion from petroleum ether two solid acid fractions were obtained as mentioned by the concerned authors, one melting at 69° and the other at 53° C. But the saponification equivalents were found to be much higher than those recorded for them by those authors and also indicated that they were mixtures. By careful fractionation using barium acetate, fraction A was found to consist of arachidic and stearic acids and fraction B stearic and palmitic acids. The remaining portion (liquid) which the previous workers called oil "X" was esterified and the methyl esters fractionated. From a careful study of the various fractions they were found to consist of mixtures of liquid (oleic and linolic) and solid (palmitic and stearic) fatty acids. None of them gave any solid acids corresponding to the description of acids "C" and "D". The fractions obtained by us did not exhibit any optical activity. Consequently our experiments do not support the contention of Khuda, Ghosh and Mukherjee. On the other hand, when the same sample of oil was analysed using well-established technique of oil study and effecting the separation of the solid and liquid acids by the lead salt alcohol method, it was found to have the following percentage composition: palmitic 13·8, stearic 18·2, arachidic 1·8, oleic 52·6 and linoleic 13·6. Our results support the conclusions of Hilditch and Murthi[7] that except in palmitic acid content the seed fat of *Azadirachta indica* may be less constant in fatty acid composition than usually obtained in the same species of plants. They agree more closely with those of Child and Ramanathan. This may be due to the fact that the concerned samples were obtained from localities having almost similar climatic conditions.

Experimental

Search for the New Acids.—450 g. of Neem oil were subjected to steam distillation employing a water-bath to heat the flask in order to minimise decomposition. The oil was subsequently extracted with hot water five times and 400 g. of the purified oil were hydrolysed by heating on a gently boiling water-bath with 200 g. of potassium hydroxide and 1000 c.c. of alcohol for 10 hours. The soap was collected and decomposed by treatment with dilute sulphuric acid when a semi-solid mass of the mixture of fatty acids floated on the top. This was separated from the aqueous layer and cooled. After standing for some time the mixture of solid and liquid fatty acids was filtered under suction. The solid residue left on the filter was triturated with petroleum ether and cooled to about 25° and filtered. It was purified by recrystallising from petroleum ether a number of times. It then melted at 69° C. and had a sap. eq. of 287·0. This corresponded to acid " A ". The petroleum mother-liquor when concentrated and cooled to 15° C. yielded another fraction which after recrystallisation from the same solvent was found to melt at 53° C. and had a sap. eq. of 264·0. This corresponded to acid " B ". The two fractions were separately examined by dissolution in alcohol and fractional precipitation using barium acetate. Each fraction of the barium salt was separately decomposed and the solid acid obtained was examined for its melting point and sap. eq. From these data it was proved that " A " and " B " were mixtures and that they contained arachidic, stearic and palmitic acids (Table III).

TABLE III

Fraction		M.P.	Sap. Eq.	Acids identified
		°C.		
"A"	1	72·5	304·6	Arachidic and stearic
	2	66·5	281·2	Stearic and palmitic
	3	60·0	275·3	Stearic and palmitic
"B"	4	58·0	264·0	Stearic and palmitic
	5	61·5	257·2	Palmitic

The liquid portion obtained by the filtration of the mixed fatty acids and corresponding to oil " X " was esterified with methyl alcohol and sulphuric acid. For this purpose 60 g. of the acids were mixed with 200 c.c. of methyl alcohol and 10 c.c. of concentrated sulphuric acid and heated on a water-bath for seven hours. The alcohol was then distilled off, the esters were taken up in ether, washed free from acid and recovered by distilling off the solvent. The liquid was found to have an I.V. of 76·3 and a mean

M.Wt. of 281·3. It was subjected to distillation at 2 mm. pressure and collected in five fractions. Each fraction was analysed for Iodine and Sap. values and the component fatty acids identified by oxidation of the fraction and separation of the acids obtained. The results are presented in Table IV. It is clear that considerable amounts of saturated acids are present in oil "X".

TABLE IV

Total Weight of Ester Distilled 57·0 *g.*

Temperature of still head	Wt. of Fraction	Sap. Eq.	I. V.	Acids identified
°C.	g.			
135–42	7·2	285·2	67·2	Palmitic and oleic
150–52	13·0	290·3	74·2	Stearic and oleic
152–54	15·0	293·6	81·4	Stearic, oleic and linoleic
154–55	12·0	293·4	98·7	Stearic, oleic and linoleic
Residue	9·8	296·7	72·2	Stearic, oleic and linoleic

Analysis of the Sample of Oil for Fatty Acid Composition.—450 g. of a fresh sample of oil was subjected to steam distillation and extraction with water. The resulting sample was saponified using standard conditions. 400 g. of the oil were employed with 250 g. of potassium hydroxide and 2500 c.c. of 95% alcohol and saponified for a duration of six hours. After distilling off the alcohol the soap was dried and extracted with ether to remove the unsaponifiable matter. It was then decomposed with dilute sulphuric acid, the mixed fatty acids were taken up in ether and washed with water. After removing the solvent, 374·0 g. of the mixed fatty acids were obtained. The solid and liquid acids were separated by the lead salt alcohol method using the procedure of Hilditch.[8] Particulars of these fractions obtained from 260 g. of mixed fatty acids are given below.

	Wt.	% by Wt.	Sap. Eq.	I. V.
Solid acids ..	117·4	32·6	276·4	2·8
Liquid acids ..	242·6	67·4	283·1	103·6

100 g. of solid acids and 200 g. of liquid acids were esterified with methyl alcohol and sulphuric acid and the properties of the esters examined.

	Wt.	Sap. Eq.	I. V.
Esters of solid acids ..	98·6	288·9	3·4
Esters of liquid acids ..	196·5	296·3	102·6

The results obtained by the fractional distillation of the esters at 2 mm. pressure and by the analysis of the various fractions are presented in Table V.

TABLE V

	Still head temperature	Wt. of fraction in g.	Saponification equivalent	Iodine Value	Acids identified and quantities obtained in g.		
					Palmitic	Oleic	Linoleic
	°C.						
1	140–150	7·3	292·1	83·9	1·1	5·6	0·6
2	150–152	11·4	295·8	99·6	nil	10·2	1·2
3	152	13·2	295·7	101·0	nil	11·6	1·6
4	152–154	13·6	295·6	108·7	nil	10·8	2·8
5	154–158	8·7	295·4	115·1	nil	6·3	2·4
6	Residue	5·8	294·8	144·9	nil	2·3	3·5
	Total weight ..	60·0	..	..	1·1	46·8	12·1
	Calculated on 67·4 g. of liquid acids	67·4	..	..	1·2	52·6	13·6

	Still head temperature °C.	Wt. of fraction in g.	Saponification equivalent	Iodine Value	Acids identified and quantities obtained in g.		
					Palmitic	Stearic	Arachidic
1	105–140	4·5	272·7	2·1	4·1	0·4	nil
2	140–142	8·6	277·8	3·4	6·2	2·4	nil
3	145–150	11·3	284·4	4·6	5·5	5·8	nil
4	152	12·8	296·2	3·1	0·8	12·0	nil
5	Residue	5·8	309·7	2·9	nil	3·4	2·4
	Total ..	43·0	..	..	16·6	24·0	2·4
	Calculated for 32·6 g. of solid acids	32·6	..	..	12·6	18·2	1·8

The following is the summary of the data relating to the fatty acid composition of the Neem oil (Table VI).

TABLE VI

	Solid Acids (32·6%) by wt.	Liquid Acids (67·4%) by wt.	Component fatty acids of the oil (% by wt.)
Palmitic	12·6	1·2	13·8
Stearic	18·2	..	18·2
Arachidic	1·8	..	1·8
Oleic	..	52·6	52·6
Linoleic	..	13·6	13·6

Summary

The work of Khuda *et al.* relating to the isolation of new fatty acids from Neem oil has been examined and their experiments repeated as far as possible. No confirmation could be obtained for the discovery of new acids. Examination of the oil by the standard methods corroborates the results of former workers.

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STUDIES IN THE CYCLOHEXANE SERIES

Part VI. The Stereoisomeric Forms of 4-Methyl-, and 3-Methylcyclohexane-1: 1-Dicarboxylic Acids and a Conclusive Chemical Evidence for the Multiplanar Cyclohexane Ring

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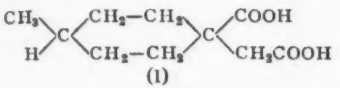
Received November 4, 1941

WHILE summing up the position of the vexed question of the chemical evidence for the multiplanar forms of the cyclohexane derivatives in Part V of this series,[1] we came to the conclusion that conclusive evidence was still lacking. Vogel and co-workers[2] have tried to advance physical evidence such as boiling point, density, and refractive index in favour of the boat and arm-chair forms of the methylcyclohexane ring, but these observations have been challenged and contradicted by Wibaut and others.[3] We do not wish to comment anything on the amazing but unconfirmed claims of Qudart-i-khuda and Co-workers[4] because we are publishing a separate paper on this subject as we have convinced ourselves that none of their claims stands the tests of experimental verifications.

Contradictory to the observations of Qudart-i-khuda,[5] Desai, Hunter, Khan and Sahariya[6] showed that it was possible to isolate 1-carboxy-4-methylcyclohexane-1-acetic acid (I) only in two isomeric forms, and assumed that these represented the *cis* and *trans* forms of the acid containing the uniplanar cyclohexane ring. However, there is the possibility of these two acids being the stable modifications derived from the *boat* and *arm-chair* forms of the multiplanar six-membered ring. With a view to getting evidence on this point, we brominated one of the isomeric forms of the acid (I) by the Hell-Volhard-Zelinsky method, and converted the monobromo acid (II) into the hydroxy derivative (III) which, on oxidation with alkaline potassium permanganate gave 4-methylcyclohexane-1 : 1-dicarboxylic acid (IV). The second isomeric form of the acid (I) furnished, under identical conditions a new isomeric 4-methylcyclohexane-1 : 1-dicarboxylic acid (IV). Similarly the two isomeric forms of 1-carboxy-3-methylcyclohexane-1-acetic acid (V) gave a pair of isomeric 3-methylcyclohexane-1: 1-dicarboxylic acid (VI).

The isolation of pairs of isomeric 4-methyl-, and 3-methylcyclohexane-1:1-dicarboxylic acids is the first conclusive chemical evidence in favour of the strainless forms of the cyclohexane ring, though fifty years have elapsed since the theoretical predictions of Sachse.[7] Despite the completion of this work in the summer of 1938, and the appearance of the preliminary note by us,[8] in *Nature*, the detailed publication was hitherto delayed owing to unavoidable circumstances.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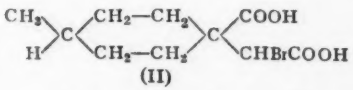
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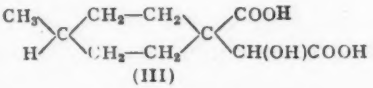
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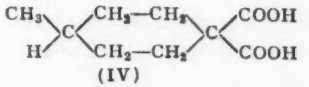
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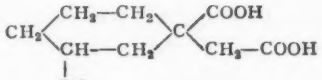
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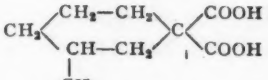
(VI)

Experimental

The isomeric forms of 1-carboxy-4-methylcyclohexane-1-acetic acid and 1-carboxy-3-methylcyclohexane-1-acetic acid were prepared by the method already described by Desai, Hunter, Khan and Sahariya (*loc. cit.*).

Bromination of 1-*Carboxy*-4-*methylcyclohexane*-1-*acetic Acid* (*A*), *m.p.* 173 *and formation of* 1-*Carboxy*-4-*methylcyclohexane*-1-α-*bromacetic acid* (*A*).—Phosphorous pentachloride (21 g.) was slowly added to the above acid (10 g.) contained in a round bottom flask with constant cooling and shaking and the mixture was warmed on the water-bath till the evolution of hydrogen chloride ceased (6 hours). After adding bromine (3 c.c.) in three lots to the cooled mixture (6 hours) and a crystal of iodine, the mixture was left overnight at the room temperature, exposed to bright sunlight for 6 hours, and finally warmed at 50–60° under reflux for 36 hours. The cooled bromo-acid chloride was poured into anhydrous formic acid (100 c.c.) and the decomposition of the acid chloride was completed by warming on the water-bath for 3–4 hours, after the initial vigour of the reaction had abated. The crude *bromo-acid* which separated out on cooling was refluxed with hexane and finally crystallised from benzene when white plates, m.p. 152°, were obtained. (Found: Br, 28·5; $C_{15}H_{20}O_4Br$ requires Br, 28·7 per cent.)

The β-*lactone* of 1-carboxy-4-methyclylclohexane-1-glycollic acid was deposited in long, white needles, m.p. 110° (previous sintering) when the

above hexane solution was kept at the room temperature after concentration. (Found: C, 60·8; H, 7·1; $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1 per cent.).

The Aniline Salt prepared by adding the above lactonic acid (1·5 g.) to the benzene solution (5 c.c.) of aniline (1·5 g.) separated out in white, tiny needles, m.p 160°. (Found: C, 62·4; H, 7·6; $C_{16}H_{21}O_4N$, H_2O requires C, 62·1; H, 7·4 per cent.).

Action of Sodium Carbonate Solution on the Bromo-acid (A) and Formation of 1-Carboxy-4-methylcyclohexane-1-glycollic acid (A).—The bromo-acid (5 g.) was neutralised with 2 N-sodium carbonate solution (20 c.c.), and then heated on the sand-bath under reflux for four hours. The alkaline solution was concentrated to a small bulk, cooled in ice, acidified with concentrated hydrochloric acid, saturated with ammonium sulphate and extracted with ether (thrice). The dried ethereal solution gave, on the removal of the solvent, *the acid* which solidified in a vacuum to a white solid, and crystallised from benzene in white scales, m.p. 134°. [Found: C, 55·6; H, 7·6; equiv.= 107·8; $C_{10}H_{16}O_5$ requires C, 55·6; H, 7·4 per cent.; equiv. = 108 (dibasic).]

Oxidation of 1-Carboxy-4-methylcyclohexane-1-glycollic Acid (A) by Alkaline Potassium Permanganate to 4-Methycyclohexane-1: 1-dicarboxylic Acid (A).—A solution of potassium permanganate (4 g.) in water (500 c.c.) was slowly added during 4 hours to the aqueous solution of the glycollic acid (2 g.) neutrallised with N/20 barium hydroxide solution. After allowing the mixture to stand for 15 hours at the room temperature, the excess of potassium permanganate was destroyed with sulphur dioxide, and the filtered solution after being made alkaline with caustic soda solution was concentrated, acidified with concentrated hydrochloric acid, saturated with ammonium sulphate, extracted with ether (thrice), dried and the acid recovered. The recovered acid which solidified immediately crystallised from benzene in small plates, m.p. 170° (effer.), and did not react with -phenylene-diamine, semicarbazide acetate and *p*-nitrophenylhydrazine showing the absence of a keto group. [Found: C, 57·6; H, 7·7; equiv. = 93·4; $C_9H_{14}O_4$ requires C, 58·1; H, 7·5 per cent.) equiv. = 93·0 (dibasic).]

Bromination of 1-Carboxy-4-methylcyclohexane-1-acetic Acid (B), m.p. 137°, and Formation of 1-Carboxy-4-methylcyclohexane 1-α-bromacetic Acid (B).—This was carried out by following all the details of the acid (A). The crude bromo-acid (m.p. 128–30°) crystallised from benzene in white rectangular plates, m.p. 132°. (Found: Br, 28·5; $C_{10}H_{15}O_4Br$ requires Br, 28·7 per cent.)

1-*Carboxy*-4-*methylcyclohexane*-1-*glycollic Acid* (*B*).—Obtained by the action of sodium carbonate on the bromo-acid (*B*) crystallised from benzene in white scales, m.p. 138° (depressed to 115° by admixture with 1-carboxy-4-methylcyclohexane-1-acetic acid (*B*), m.p. 137°. (Found: C, 55·2; H, 7·5; $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·4 per cent.)

4-*Methylcyclohexane*-1 : 1-*dicarboxylic Acid* (*B*).—Prepared by oxidising the above glycollic acid (B) crystallised from benzene in white, rectangular plates, m.p. 175° (effer.), depressed by admixture with 4-methylcyclohexane-1: 1-dicarboxylic acid (A) to 148°, and gave negative tests for the keto-acid. [Found: C, 57·7; H, 7·4; equiv. = 93·5; $C_9H_{14}O_4$ requires C, 58·1; H, 7·5; equiv. = 93·0 (dibasic).]

Derivatives of 1-*Carboxy*-3-*methylcyclohexane*-1-*acetic Acid* (*A*), *m.p.* 163°, *and* 1-*Carboxy*-3-*methylcyclohexane*-1-*acetic Acid* (*B*), *m.p.* 108-09°), 1-*Carboxy*-3-*methylcyclohexane*-1-α-*brom-acetic Acid* (*A*), prepared in the usual manner, crystallised from benzene in white plates, m.p. 142°. (Found: Br, 28·6; $C_{10}H_{15}O_4Br$ requires Br, 28·7 per cent.)

1-*Carboxy*-3-*methylcyclohexane*-1-*glycollic Acid* (*A*), crystallised from benzene in white scales, m.p. 166°. (Found: C, 55·4; H, 7·5; $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·4 per cent.)

3-*Methylcyclohexane*-1: 1-*dicarboxylic acid* (*A*), crystallised from benzene in plates, m.p. 171–72° (effer.), and gave all the negative tests for the keto-acid. [Found: C, 57·8; H, 7·5; equiv. = 93·3; $C_9H_{14}O_4$ requires C, 58·1; H, 7·5 per cent., equiv. = 93·0 (dibasic).]

1-*Carboxy*-3-*methylcyclohexane*-1-α-*bromacetic acid* (*B*), crystallised from benzene in white plates, m.p. 155°. (Found: Br, 28·5; $C_{10}H_{15}O_4Br$ requires Br, 28·7 per cent.)

1-*Carboxy*-3-*methylcyclohexane*-1-*glycollic acid* (*B*), crystallised from benzene in white scales, m.p. 134°. [Found: C, 55·4; H, 7·4; equiv. = 109.0; $C_{10}H_{16}O_5$ requires C, 55·3; H, 7·4 per cent.; equiv. = 108 (dibasic).]

3-*Methylcyclohexane*-1: 1-*dicarboxylic acid* (*B*), crystallised from benzene in white, rectangular plates, m.p. 185° (effer.), and did not respond to the tests for the keto-acid. [Found: C, 58·2; H, 7·6; $C_{19}H_{14}O_4$ requires C, 58·1; H, 7·5 per cent.).]

Summary

A pair of stereo-isomeric 4-methylcyclohexane-1: 1-dicarboxylic acids has been prepared from a pair of isomeric 1-carboxy-4-methylcyclohexane-1-acetic acids. Similarly two isomeric 3-methylcyclohexane-1: 1-dicarboxylic

acids have been obtained from the two isomeric 1-carboxy-3-methylcyclohexane-1-acetic acids. These results supply the first convincing proof of the multiplanar forms of the cylohexane ring.

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ON ALGEBRAIC IRRATIONALS

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§1. Let $[x]$ denote the integral part of x;

$$\{x\} = x - [x] - \frac{1}{2};$$

and

$$S(\theta, n) = \sum_{r=1}^{n} \{r\theta\}.$$

In their paper "Some problems of Diophantine approximation" published in *Proc. London Math. Soc.* (2), 20 (1922), Hardy and Littlewood prove by a transcendental method that, if θ is algebraic, then there is a constant $\beta < 1$ such that

$$S(\theta, n) = 0(n^{\beta}). \tag{1}$$

The object of this note is to derive the above from a result in the same paper, proved by an elementary method. For the sake of completeness, I prove all the results.

The following notations are used:

$$\theta = x_1 = a_1 + \frac{1}{x_2};\ x_2 = a_2 + \frac{1}{x_3}, \cdots, x_r = a_r + \frac{1}{x_{r+1}},$$

where $a_r = [x_r]$; $\frac{p_n}{q_n}$ is the n th convernt.

$$n_2 = \left[\frac{n}{x_2}\right] = \frac{n}{x_2} - \delta_2;\ n_3 = \left[\frac{n_2}{x_3}\right] = \frac{n_2}{x_3} - \delta_3; \cdots$$

$$n_r = \left[\frac{n_{r-1}}{x_r}\right] = \frac{n_{r-1}}{x_r} - \delta_r.$$

$$k = \frac{1}{2^{(k-1)/2}}.$$

§2. Lemma (1): $x_2 x_3 \cdots x_r = x_r \cdot q_{r-1} + q_{r-2}$.

Let the result be true when $r = n$. Then

$$x_2 \cdots x_n x_{n+1} = x_{n+1}(x_n \cdot q_{n-1} + q_{n-2})$$

$$= x_{n+1} a_n q_{n-1} + \frac{q_{n-1}}{x_{n+1}} + q_{n-2} = x_{n+1} q_n + q_{n-1}.$$

Further $q_1 = 1$, $q_2 = a_2$, so that, since $x_2 = a_2 + \frac{1}{x_3}$, we have,

$$x_2 x_3 = x_3 a_2 + 1 = x_2 q_2 + q_1.$$

Thus we get the result by induction.

LEMMA (2): When $r \geq 2$, $q_n > 2^{r/2} \cdot q_{n-r}$.

Now, $q_n \geq q_{n-1} + q_{n-2} = (a_{n-1}+1)\, q_{n-2} + q_{n-3}$

$> 2q_{n-2} + q_{n-3} > 3q_{n-3} > 2^{3/2} \cdot q_{n-3}$.

So we get the result by alternate induction.

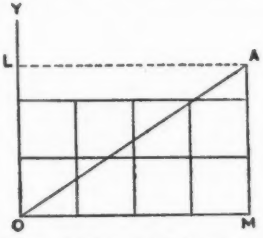
LEMMA (3): (Lerche's formula): If n is a positive integer; θ is a positive irrational;

$$n\theta = [n\theta] + \delta;\ S = \sum_1^n \{\mu\theta\};\ S' = \sum_1^{n\theta} \left\{\frac{\nu}{\theta}\right\};$$

then
$$S + S' = \frac{1}{2}\delta - \frac{\delta(1-\delta)}{2\theta}.$$

This formula was given without proof by Lerch, and derived from a more general formula by Hardy and Littlewood. Though the proof given below is based on theirs, it is direct and simple.

In the figure, OA is the line $y = x\theta$, and $OM = n$. Since θ is irrational, the origin is the only lattice point on OA. Let N, N′ denote the number of



lattice points in the triangles OMA, OLA respectively, omitting those on the axes.

Then, $$N = \sum_1^n [\mu\theta] = \sum_1^n \left(\mu\theta - \{\mu\theta\} - \frac{1}{2}\right) = \frac{1}{2}n(n+1)\,\theta - \frac{1}{2}n - S.$$

$$N' = \sum_1^{n\theta} \left[\frac{\nu}{\theta}\right] = \sum_1^{n\theta} \left(\frac{\nu}{\theta} - \left\{\frac{\nu}{\theta}\right\} - \frac{1}{2}\right)$$

$$= \frac{1}{2\theta}[n\theta]\,([n\theta]+1) - \frac{1}{2}[n\theta] - S'$$

$$= (n\theta - \delta)\frac{(n\theta - \delta + 1)}{2\theta} - \frac{1}{2}(n\theta - \delta) - S'$$

$$= \frac{1}{2}n^2\theta - n\delta + \frac{1}{2}\delta - \delta\frac{(1-\delta)}{2\theta} - \frac{1}{2}n\theta + \frac{1}{2}n - S'.$$

So,
$$N + N' = n^2\theta - n\delta + \frac{1}{2}\delta - \delta\frac{(1-\delta)}{2\theta} - S - S'. \qquad (2)$$

But from the figure,

$$N + N' = n\,[n\theta] = n\,(n\theta - \delta) = n^2\theta - n\delta. \tag{3}$$

Subtracting (3) from (2), we get that

$$S + S' = \frac{1}{2}\,\delta - \delta\,\frac{(1-\delta)}{2\theta}.$$

LEMMA (4) (Hardy and Littlewood):

$$S\,(\theta, n) = 0\,(x_2 + \cdots + x_r) + 0\left(\frac{n}{x_2 \cdots x_r}\right).$$

From lemma (3), $S\,(\theta, n) + S\left(\frac{1}{\theta}, n\theta\right) = 0\left(\frac{1}{\theta}\right)$.

So
$$S\,(\theta, n) = S\,(x_1, n) = S\left(a_1 + \frac{1}{x_2}, n\right) = S\left(\frac{1}{x_2}, n\right)$$
$$= 0\,(x_2) - S\left(x_2, \frac{n}{x_2}\right) = 0\,(x_2) - S\,(x_2, n_2)$$
$$= 0\,(x_2) - S\left(a_2 + \frac{1}{x_3}, n_2\right) = 0\,(x_2)\,0\,(x_3) - S\left(\frac{1}{x_3}, n_2\right)$$
$$= 0\,(x_2) + 0\,(x_2) + S\,(x_3, n_3) = \cdots$$
$$= 0\,(x_2 + \cdots + x_r) \pm S\,(x_r, n_r)$$
$$= 0\,(x_2 + \cdots + x_r) + 0\left(\frac{n}{x_2 \cdots x_r}\right).$$

§ 3. THEOREM A: *If there are positive constants* A, h *such that*

$$\left|\theta - \frac{p}{q}\right| > \frac{A}{q^h} \text{ for } \textit{all } q,$$

$h > 2$, *and* $\alpha = \left(\frac{h-2}{h-1}\right)$, *then*

$$S\,(\theta, n) = 0\,(n^\alpha).$$

Now $\frac{A}{q_s^h} < \left|\theta - \frac{p_s}{q_s}\right| < \frac{1}{x_{s+1} \cdot q_s^2}$, so that

$$x_{s+1} = 0\,(q_s^{h-2}), \tag{4}$$

Choose r so that

$$x_2 x_3 \cdots x_{r+1} > n^{1/(h-1)} > x_2 \cdots x_r. \tag{5}$$

So, from lemma (1),

$$q_r = 0\,(x_r q_{r-1}) = 0\,(x_2 \cdots x_r) = 0\,(n^{1/(h-1)}). \tag{6}$$

Then, from (4), (6),

$$x_2 + x_3 + \cdots + x_{r+1} = 0\,(q_1^{h-2} + q_2^{h-2} + \cdots + q_r^{h-2})$$
$$= 0\,(q_r^{h-2})\,(1 + 1 + k + k^2 + k^3 + \cdots) = 0\,(q_r^{h-2}) = 0\,(n^\alpha). \tag{7}$$

Again from (5),

$$\frac{n}{x_2 \cdots x_{r+1}} = 0\left(\frac{n}{n^{1/(k-1)}}\right) = 0\,(n^{\epsilon}). \tag{8}$$

From (7), (8), and lemma (4), we get the theorem.

THEOREM B: *When θ is algebraic and of degree* r,

$$S(\theta, n) = 0\,(n^{\beta}), \text{ where } \beta = \left(\frac{2\sqrt{r}-2}{2\sqrt{r}-1}\right).$$

This follows from Theorem A and Siegel's theorem (Hardy and Littlewood prove this with $\beta + \epsilon$ instead of β).

ON A PROBLEM IN DIOPHANTINE APPROXIMATION

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§ 1. *Introduction*

1·1. Let

(1) $[x]$ denote the integral part of x;

(2) $\{x\}=x-[x]-\frac{1}{2}$ when x is not an integer, and $\{x\}=0$ when x is an integer;

(3) $S(x, N)=\sum_{n=1}^{N}\{nx\}$;

(4) a_n, x_n be respectively the nth partial and complete quotients to the simple continued fraction for the positive irrational θ; and $\frac{p_n}{q_n}$ the nth convergent;

(5) $\sigma(n)=a_1+a_2+\cdots+a_n$;

(6) $f_n=\frac{(-1)^{n+1}}{q_n(x_{n+1}q_n+q_{n-1})}$;

(7) $t_n=\frac{q_{n-2}}{q_{n-1}}$;

(8) $F_n=F_n(h)=\frac{h+\frac{2N_1+1}{q_{n-1}}}{x_n+t_n}$;

(9) $h_n=\left[\frac{a_n}{2}\right]$ when $a_n\geqslant 2$, and $h_n=1$ when $a_n=1$;

(10) k denote the number of a_r with the suffix $r\leqslant n$ for which $a_r=a_{r+1}=1$;

(11) $(p, q)=1$;

(12) $b_n=a_n-1$ when $a_n\geqslant 2$, and $b_n=\frac{2}{a_{n+1}+1\cdot 5}$ when $a_n=1$.

1·2. The function $S(\theta, N)$ has been considered by Lerch, Weyl, Hardy and Littlewood, Ostrowski, and Hardy. In their P.L.M.S. paper, Hardy and Littlewood prove several results about this function, and state without

proof several others. In this paper I establish an interesting reduction formula for $S(\theta, N)$, and with the help of it, besides establishing all the results about $S(\theta, N)$ mentioned in the above paper, I prove a few more new results also. It may be observed that all the proofs are easy and elementary. The reduction formula turns out to be well suited to the study of the function.

The reduction formula is the following:—

If $$q_{n-1} \leqslant N < q_n, \text{ and } N = hq_{n-1} + N_1,$$

then $$S(\theta, N) = S(\theta, N_1) + \frac{1}{2}(-1)^{n-1} h (1 - F_n).$$

One result seems to be worth observing even at this stage. In a sense, $\sigma(n)$ is the true measure of $S(\theta, N)$. As a matter of fact, it is proved that, when $q_{n-1} \leqslant N < q_n$,

$$|S(\theta, N)| \leqslant \frac{1}{2}\sigma(n) \text{ for all } N,$$

and $$|S(\theta, N)| \geqslant \frac{1}{32}\left(\sigma(n) - n + \frac{k}{5}\right)$$

for an infinity of values of N.

This being the case, the determination of best possible constants in the above inequalities is a problem of considerable interest.

The definition given above for $\{x\}$ is adopted from Question number, 1802 in the *Mathematics Student*, by Amritha Sagar Puri, and the question had some part in my getting the reduction formula. When x is irrational $S(x, N)$ is the same.

§ 2. *Lemmas*

LEMMA (1): *When* $r > 2$, $q_{n-r} < q_n/2^{r/2}$.

Now, $$q_n = a_n q_{n-1} + q_{n-2} = (a_n a_{n-1} + 1) q_{n-2} + a_n q_{n-3}$$
$$\geqslant 2q_{n-2} + q_{n-3} = 2(a_{n-2} q_{n-3} + q_{n-4}) + q_{n-3}$$
$$\geqslant 3q_{n-3} > 2^{3/2} q_{n-3}.$$

Hence $q_{n-2} < q_n/2^{2/2}$, and $q_{n-3} < q_n/2^{3/2}$.

Thus we get the lemma by induction.

LEMMA (2): $1 + a_2 + a_3 + \cdots + a_n \leqslant q_n$, *when* $n > 5$.

$$q_5 = a_5 q_4 + q_3 = a_5(a_4 q_3 + q_2) + a_3 q_2 + 1$$
$$\geqslant a_5 + 1 + a_4 q_3 + a_3 q_2 = a_5 + 1 + a_4(a_3 + q_2) + a_3 a_2$$
$$\geqslant a_5 + 1 + a_3 + a_4 + a_2.$$

Let the result be true for n.

Then $q_{n+1} \geqslant a_{n+1} \cdot q_n + 1 \geqslant a_{n+1}(a_n + \cdots + a_2 + 1) + 1$

$$\geqslant a_{n+1} + \cdots + a_2 + 1.$$

So we get the result by induction.

LEMMA (3): $(1 + a_1) \cdots (1 + a_n) > q_n > a_1 \cdot a_2 \cdots a_n$.

$$q_n = a_n q_{n-1} + q_{n-2} \leqslant (1 + a_n)\, q_{n-1}$$

and $$q_n \geqslant a_n q_{n-1}.$$

LEMMA (4): $S\left(\frac{p}{q}, q\right) = 0$.

Since $(p, q) = 1$, the remainders $r_1, r_2, \cdots, r_{q-1}$, when we divide $p, 2p, \cdots, (q-1)\,p$ by q, are the numbers $1, 2, \cdots, q-1$ in a certain order. Hence

$$S\left(\frac{p}{q}, q\right) = \sum_{1}^{q} \left\{\frac{np}{q}\right\} = \sum_{1}^{q-1} \left(\frac{r_n}{q} - \frac{1}{2}\right)$$

$$= \frac{1}{q}(1 + 2 + \cdots + q - 1) - \frac{1}{2}(q-1) = 0.$$

LEMMA (5): $S\left(\frac{p}{q}, mq\right) = 0$.

Now,
$$S\left(\frac{p}{q}, mp\right) = \sum_{r=0}^{m-1} \sum_{t=1}^{q} \left\{\frac{(rq+t)\,p}{q}\right\}$$

$$= \sum_{r} \sum_{t} \left\{\frac{tp}{q}\right\} = \sum_{r} S\left(\frac{p}{q}, q\right) = 0.$$

LEMMA (6): $S\left(\frac{p}{q}, mq + r\right) = S\left(\frac{p}{q}, r\right)$.

From Lemma (5),

$$S\left(\frac{p}{q}, mq + r\right) = S\left(\frac{p}{q}, mq + r\right) - S\left(\frac{p}{q}, mq\right)$$

$$= \sum_{t=1}^{r} \left\{\frac{(mq+t)\,p}{q}\right\} = \sum_{t=1}^{r} \left\{\frac{tp}{q}\right\} = S\left(\frac{p}{q}, r\right).$$

LEMMA (7): *If* $r < q_{n+1}$, *then* $\{r\theta\} = \left\{\frac{rp_n}{q_n}\right\} + rf_n$ *when* r *is not a multiple of* q_n, *and* $\{r\theta\} = rf_n + \frac{1}{2}(-1)^n$ *when* r *is a multiple of* q_n.

Now $r < q_{n+1} = a_{n+1} q_n + q_{n-1} < x_{n+1} q_n + q_{n-1}$.

So
$$|rf_n| = \frac{r}{q_n (x_{n+1} q_n + q_{n-1})} < \frac{1}{q_n}.$$

(a) r is not a multiple of q_n.

Then $$\frac{1}{q_n} \leqslant \frac{rp_n}{q_n} - \left[\frac{rp_n}{q_n}\right] \leqslant \frac{q_n - 1}{q},$$

so that $$0 < \frac{rp_n}{q_n} - \left[\frac{rp_n}{q_n}\right] + rf_n < 1.$$

So the fractional part of $\frac{rp_n}{q_n} + rf_n$ is equal to the sum of rf_n and the fractional part of $\frac{rp_n}{q_n}$.

Hence, since $\theta = \frac{p_n}{q_n} + f_n$,

$$\{r\theta\} = \left\{\frac{rp_n}{q_n}\right\} + rf_n.$$

(b) r is a multiple of q_n.

Then $\{r\theta\} = \left\{\frac{rp_n}{q_n} + rf_n\right\} = \{1 + rf_n\} = rf_n + \frac{1}{2}(-1)^n$; because, when $n+1$ is odd, f_n is negative, and so $1 + rf_n - [1 + rf_n] = 1 + rf_n$; and when $n+1$ is even, f_n is positive and so

$$1 + rf_n - [1 + rf_n] = rf_n.$$

§ 3. *The Reduction Formula and Corollaries*

3·1. THEOREM I: *When* $q_{n-1} \leqslant N < q_n$, *and* $N = hq_{n-1} + N_1$, *where* $N_1 < q_{n-1}$,

$$S(\theta, N) = S(\theta, N_1) + \frac{1}{2}(-1)^{n-1} h (1 - F_n).$$

From lemma (7) and the formula $\theta = \frac{p_{n-1}}{q_{n-1}} + f_{n-1}$,

$$S(\theta, N) = S\left(\frac{p_{n-1}}{q_{n-1}}, N\right) + \frac{1}{2}(-1)^{n-1} h + f_{n-1}(1 + 2 + \cdots + N). \quad (a)$$

From lemma (6),

$$S\left(\frac{p_{n-1}}{q_{n-1}}, N\right) = S\left(\frac{p_{n-1}}{q_{n-1}}, N_1\right). \quad (b)$$

Again from lemma (7),

$$S\left(\frac{p_{n-1}}{q_{n-1}}, N_1\right) = S(\theta, N_1) - f_{n-1}(1 + 2 + \cdots + N_1). \quad (c)$$

From (a), (b), (c), we get that

$$S(\theta, N) - S(\theta, N_1) = \frac{1}{2}(-1)^{n-1} h + f_{n-1}(N_1 + 1 + N_1 + 2 + \cdots + N)$$

$$= \frac{1}{2}(-1)^{n-1} h + \frac{1}{2} f_{n-1}[N(N+1) - N_1(N_1+1)]$$

$$= \frac{1}{2}(-1)^{n-1} h + \frac{1}{2} f_{n-1} [h^2 q_{n-1}^2 + h q_{n-1} (2N_1 + 1)]$$

$$= \frac{1}{2}(-1)^{n-1} h \left(1 - \frac{h + \frac{2N_1+1}{q_{n-1}}}{x_n + \frac{q_{n-2}}{q_{n-1}}} \right)$$

$$= \frac{1}{2}(-1)^{n-1} h (1 - F_n).$$

3·2. COROLLARY (1):

$$|S(\theta, N) - S(\theta, N_1)| \leqslant \frac{1}{2} h = \frac{1}{2}\left[\frac{N}{q_{n-1}}\right] \leqslant \frac{1}{2} a_n.$$

When $h < a_n - 1$,

$$F_n < \frac{a_n - 1 + 2}{a_n} = \frac{a_n + 1}{a_n} \leqslant 2.$$

When $h = a_n$, since $N < q_n$, $N_1 \leqslant q_{n-2} - 1$.

So $$F_n < \frac{a_n + 2t_n}{a_n + t_n} < 2.$$

In any case, $0 < F_n < 2$, so that $|1 - F_n| < 1$.

Hence the corollary follows from theorem I.

COROLLARY (2): *When* $q_{n-1} \leqslant N < q_n$,

$$|S(\theta, N)| \leqslant \frac{1}{2}\left(\frac{N}{q_{n-1}} + a_{n-1} + a_{n-2} + \cdots a_2\right)$$

From corollary (1),

$$|S(\theta, N)| \leqslant |S(\theta, N_1)| + \frac{1}{2}\frac{N}{q_{n-1}}$$

If $q_{s-1} \leqslant N_1 < q_s$, where $s \leqslant n-1$, putting $N_1 = h' q_{s-1} + N_2$, where $N_2 < q_{s-1}$, we get that

$$|S(\theta, N_1)| \leqslant |S(\theta, N_2)| \leqslant \frac{1}{2} a_{s-1} \leqslant \frac{1}{2} a_{n-1}.$$

Proceeding like this, at most after $n-2$ steps, we get that

$$|S(\theta, M_2)| \leqslant \frac{1}{2} a_2, \text{ where } M_2 < q_2.$$

By adding, we get the corollary.

THEOREM II: *When* $q_{n-1} \leqslant N < q_n$,

$$|S(\theta, N)| \leqslant \frac{1}{2}(a_2 + a_3 + \cdot + a_n) \leqslant \frac{1}{2}\sigma(n).$$

This is immediate from corollary (2).

COROLLARY (3): $S(\theta, N) = O\left(\frac{N}{q_r}\right) + O(q_r)$.

This result is a known one.

Since $a_s < \frac{q_s}{q_{s-1}}$, from corollary (2),

$$|S(\theta, N)| \leqslant \frac{1}{2}\left(\frac{N}{q_{n-1}} + \frac{q_{n-1}}{q_{n-2}} + \cdots + \frac{q_{r+1}}{q_r}\right) + \frac{1}{2}(a_r + \cdots + a_2)$$

$$\leqslant \frac{1}{2q_r}(N + q_{n-1} + q_{n-2} + \cdots + q_{r+1}) + \frac{1}{2}q_r, \text{ from lemma (2),}$$

$$\leqslant \frac{N}{2q_r}\left(1 + 1 + 1 + \frac{1^{2/2}}{2} + \frac{1^{3/2}}{2} + \cdots + \frac{1^{(r-2)/2}}{2}\right) + \frac{1}{2}q_r, \text{ from lemma (1),}$$

$$\leqslant \frac{N}{2q_r}\left(\frac{3 + \frac{1}{2}}{\left(1 - \frac{1}{\sqrt{2}}\right)}\right) + \frac{1}{2}q_r = O\left(\frac{N}{q_r}\right) + O(q_r).$$

§ 4. *Results for General* θ

THEOREM III: (Well-known). $S(\theta, N) = 0(N)$.

The proof is immediate from corollary (3). From lemma (6), we get that the result is true even when θ is rational.

THEOREM IV: *If* $h = \left[\frac{a_n}{2}\right]$ *or* 1 *according as* $a_n > 1$ *or not,* $q_{n-1} \leqslant N < q_n$, $N = hq_{n-1} + N_1$, *and* $2N_1 + 1 \leqslant q_{n-2}$, *then*

$$(-1)^{n-2}[S(\theta, N) - S(\theta, N_1)] > \frac{1}{8}b_n.$$

Since $2N_1 + 1 \leqslant q_{n-2}$,

$$F_n \leqslant \frac{h + t_n}{x_n + t_n} = 1 - \frac{x_n - h}{x_n + t_n}, \text{ and so}$$

$$1 - F_n \geqslant \frac{x_n - h}{x_n + t_n}. \tag{d}$$

(1) Let $a_n \geqslant 2$. Put $x_n = a_n + k$, so that $k < 1$.

Then $h = \left[\frac{a_n}{2}\right] = \frac{1}{2}a_n - \phi$, where $\phi \leqslant \frac{1}{2}$.

$$\frac{h}{2}(1 - F_n) > \frac{1}{2}\left(\frac{1}{2}a_n - \phi\right)\frac{(a_n + k - \frac{1}{2}a_n + \phi)}{(a_n + k + t_n)}$$

$$= \frac{\frac{1}{2}\left(\frac{1}{4}a_n^2 - \phi^2 + \frac{1}{2}ka_n - k\phi\right)}{(a_n + k + t_n)}$$

$$= \frac{1}{8}a_n - \frac{\frac{1}{8}(a_nk + a_nt_n + 4\phi^2 - 2ka_n + 4k\phi)}{(a_n + k + t_n)}$$

$$\geqslant \frac{1}{8}\, a_n - \frac{\frac{1}{8}(a_n t_n + 1 + 2k - a_n k)}{(a_n + k + t_n)}$$

$$\geqslant \frac{1}{8}\, a_n - \frac{\frac{1}{8}(a_n t_n + 1)}{(a_n + k + t_n)}$$

$$\geqslant \frac{1}{8}\, a_n - \frac{1}{8}\ ;\ \text{for } t_n \leqslant 1. \qquad (e)$$

(2) Let $a_n = 1$.

Then from (d),

$$\frac{h}{2}(1 - \mathrm{F}_n) \geqslant \frac{x_n - 1}{2(x_n + t_n)} \geqslant \frac{1 + k - 1}{2(1 + k + 1)} = \frac{k}{2(2 + k)}$$

$$= \frac{1}{2(2x_{n+1} + 1)} \geqslant \frac{1}{2(2a_{n+1} + 3)} = \frac{1}{4(a_{n+1} + 1 \cdot 5)}. \qquad (f)$$

From (e), (f) and theorem I, we get immediately the present one.

THEOREM V: *$S(\theta, N)$ changes sign infinitely often.*

In theorem IV, put $\mathrm{N}_1 = 0$. Then $(-1)^{n-1}\, \mathrm{S}(\theta, \mathrm{N}) > \frac{1}{8}\, b_n$.

Since $b_n > 0$, we get the result immediately.

THEOREM VI: *In the range (q_{n-4}, q_n), there is at least one N for which*

$$|S(\theta, N)| > \frac{1}{32}\left(\sigma(n) - n + \frac{2}{5}k\right).$$

Let $h = h(n) = \left[\frac{a_n}{2}\right]$ or 1 according as $a_n \geqslant 2$ or $=1$. Further, let

$$\mathrm{S}_n = \mathrm{S}[\theta, \mathrm{N}(n)], \text{ where}$$

$$\mathrm{N}(n) = \mathrm{N} = h_n q_{n-1} + \mathrm{N}_4,$$

$$\mathrm{N}_4 = h_{n-4}\, q_{n-5} + \mathrm{N}_8,$$

$$\mathrm{N}_8 = h_{n-8}\, q_{n-9} + \mathrm{N}_{12} \text{ and so on.}$$

Then $\mathrm{N} = h_n q_{n-1} + h_{n-4}\, q_{n-5} + \cdots$,

and from lemma (1),

$$\mathrm{N}_4 \leqslant \frac{1}{2}\, q_{n-2} - 1 \text{ and so on.}$$

Hence from theorem IV,

$$(-1)^{n-1}\, [\mathrm{S}(\theta, \mathrm{N}) - \mathrm{S}(\theta, \mathrm{N}_4)] \geqslant \frac{1}{8}\, b_n.$$

Similarly,

$$(-1)^{n-5}\, [\mathrm{S}(\theta, \mathrm{N}_4) - \mathrm{S}(\theta, \mathrm{N}_8)] \geqslant \frac{1}{8}\, b_{n-4},$$

and so on. Consequently,

$$(-1)^{n-1}\, \mathrm{S}(\theta, \mathrm{N}) \geqslant \frac{1}{8} \sum_{r=0}^{n/4} b_{n-4r}.$$

Or, in other words,

$$(-1)^{n-1} S_n \geqslant \frac{1}{8} \sum_{r=0}^{n/4} b_{n-4r}$$

In this, put $n = n$, $n-1$, $n-2$ and $n-3$. Then

$$T = (-1)^{n-1}(S_n + S_{n-2}) + (-1)^n (S_{n-1} + S_{n-3})$$

$$\geqslant \frac{1}{8} \sum_{r=1}^{n} b_r \qquad (g)$$

(1) $a_n \geqslant 2$, $a_{n+1} = 1$.

Then $b_n + b_{n+1} \geqslant a_n - 1 = a_n + a_{n+1} - 2$.

(2) $a_n = 1$, $a_{n+1} \geqslant 2$.

Then $b_n + b_{n+1} \geqslant a_{n+1} - 1 = a_n + a_{n+1} - 2$.

(3) $a_n = 1$, $a_{n+1} = 1$.

Then $b_n + b_{n+1} > b_n = \dfrac{2}{a_{n+1} + 1 \cdot 5} = \dfrac{2}{2 \cdot 5} = \dfrac{4}{5}$

$$= 2 - \frac{6}{5} = a_n + a_{n+1} - \frac{6}{5}.$$

(4) $a_n \geqslant 2$, $a_{n+1} \geqslant 2$.

Then $b_n + b_{n+1} = a_n + a_{n+1} - 2$

So if $a_n = a_{n+1} = 1$, then $b_n + b_{n+1} \geqslant a_n + a_{n+1} - \dfrac{6}{5}$

and in all other cases $b_n + b_{n+1} \geqslant a_n + a_{n+1} - 2$.

Hence $$2 \sum_{1}^{n} b_r = b_1 + b_n + \sum_{1}^{n-1} (b_r + b_{r+1})$$

$$\geqslant b_1 + b_n + \sum_{1}^{n-1} (a_r + a_{r+1} - 2) + \frac{4k}{5} \text{ (see definition 10)}$$

$$= 2 \sum_{1}^{n} a_r + \frac{4k}{5} - 2n + 2 - (a_1 - b_1) - (a_n - b_n).$$

If $a_r \geqslant 2$, $a_r - b_r = a_r - (a_r - 1) = 1$.

If $a_r = 1$ $a_r - b_r < 1$.

In any case, $a_r - b_r - 1 < 0$.

Hence $$\sum_{1}^{n} b_r \geqslant \sum_{1}^{n} a_r - n + \frac{2k}{5} = \sigma(n) - n + \frac{2k}{5}.$$

From this and (g), we get that

$$T \geqslant \frac{1}{8}\left(\sigma(n) - n + \frac{2k}{5}\right).$$

So, if $M = \text{Max.}(|S_n|, |S_{n-1}|, |S_{n-2}|, |S_{n-3}|)$, then

$$M \geqslant \frac{1}{32}\left(\sigma(n) - n + \frac{2}{5} k\right).$$

This means that in the range $(q_{n-4} \leqslant N < q_n)$, there is at least one N for which

$$|S(\theta, N)| > \frac{1}{32}\left(\sigma(n) - n + \frac{2}{5}k\right).$$

THEOREM VII: *There is an N in* (q_{n-4}, q_n) *for which*

$$|S(\theta, N)| > \frac{3}{320}\sigma(n).$$

Let m be the number of $r \leqslant n$ for which $a_r = 1$. Then

$$k \geqslant m - (n-m) - 1 = 2m - n - 1.$$

Further for $n - m$ values, $a_r \geqslant 2$.

So $$\frac{7}{10}\sigma(n) \geqslant \frac{7 \times 2}{10}(n-m) + \frac{7m}{10} = \frac{7}{5}n - \frac{7}{10}m.$$

Hence

$$\sigma(n) - n + \frac{2}{5}k = \frac{3}{10}\sigma(n) + \frac{7}{10}\sigma(n) - n + \frac{2}{5}k$$

$$\geqslant \frac{3}{10}\sigma(n) + \frac{7n}{5} - \frac{7m}{10} - n + \frac{4m}{5} - \frac{2n}{5} - \frac{2}{5}$$

$$= \frac{3}{10}\sigma(n) + \frac{m-2}{5} \geqslant \frac{3}{10}\sigma(n) + 0(1).$$

Hence from theorem VI, for a suitable N in (q_{n-4}, q_n)

$$|S(\theta, N)| \geqslant \frac{3}{320}\sigma(n) + 0(1).$$

So the theorem is proved.

THEOREM VIII (Hardy and Littlewood): *For an infinity of values of N,*

$$|S(\theta, N) > \frac{3}{320}\log N + 0(1).$$

Now,

$$\sigma(n) = a_1 + \cdots + a_n \geqslant \sum_{r=1}^{n} \log(1 + a_r)$$

$$= \log(1 + a_1)(1 + a_2) \cdots (1 + a_n) > \log q_n, \text{ from lemma (3).}$$

From theorem VII, in the range (q_{n-4}, q_n), there is an N for which

$$|S(\theta, N)| \geqslant \frac{3}{320}\sigma(n) + 0(1); \text{ hence for which}$$

$$|S(\theta, N)| \geqslant \frac{3}{320}\log q_n + 0(1) > \frac{3}{320}\log N + 0(1).$$

In their paper Hardy and Littlewood say that the settlement of the above question is the most difficult one in this connection.

§5. *Results for Algebraic* θ

THEOREM IX: *When* $\theta=\frac{p}{q}$, $S(\theta, N)=O(q)$. *Further Max.* $S(\theta, N)=\frac{q-2}{8}+\phi$ *and Min.* $S(\theta, N)=-\frac{q-2}{8}+\phi$, *where* $|\phi|<\frac{1}{q}$.

The first part follows from lemma (6). By putting $\theta=\frac{q-1}{q}$ and $\theta=\frac{1}{q}$, the other two can be very easily established.

THEOREM X: *If* a_n *be bounded so that* $a_n \leqslant K$, *there is at least one* N *in the interval* (q_{n-1}, q_n) *for which* $(-1)^{n-1} S(\theta, N) > \frac{\log N}{40 K \log (2K)}$.

For the S_n in the proof of theorem VI, when $S(\theta, N)=S_n$, we have

$$(-1)^{n-1} S(\theta, N) \geqslant \frac{1}{8} \sum_r b_{n-4r}$$

$$\geqslant \frac{1}{8} \sum_r \frac{2}{a_{n-4r+1}+1 \cdot 5} \geqslant \frac{1}{10} \sum_r \frac{1}{a_{n-4r+1}}$$

$$\geqslant \frac{1}{10} \sum_r \frac{1}{K} \geqslant \frac{n}{40K}.$$

But

$$q_n \leqslant (1+a_n) \cdots (1+a_1) \leqslant 2^n a_1 \cdots a_n \leqslant (2K)^n,$$

so that $$n > \frac{\log q_n}{\log (2K)} \geqslant \frac{\log N}{\log (2K)}.$$

Therefore,

$$(-1)^{n-1} S(\theta, N) \geqslant \frac{\log N}{40K \log (2k)}.$$

THEOREM XI: *When* θ *is quadratic, there is a constant* c *such that each of the inequalities*

$S(\theta, N) > c \log N$, *and* $S(\theta, N) < -c \log N$ *is satisfied for an infinity of values of* N.

Since a_n is bounded in this case, the theorem is an immediate consequence of theorem X.

THEOREM XII: *If there are positive constants* A *and* h *such that*

$$\left|\theta-\frac{p}{q}\right| \geqslant \frac{A}{q^h} \text{ for all } q, (p, q)=1,$$

then $S(\theta, N)=O(N^\alpha)$ *when* $h>2$, *and* $S(\theta, N)=O(\log N)$ *when* $h=2$, *where* $\alpha=\frac{(h-2)}{(h-1)}$.

Now, $\frac{A}{q_n^h} < \left|\theta - \frac{p_n}{q_n}\right| < \frac{1}{q_n q_{n+1}}$, so that

$$q_n > A^{\nu} q^{\nu}{}_{n+1}, \text{ where } \nu = \frac{1}{(h-1)}.$$

$$\text{So } a_r \leqslant \frac{q_r}{q_{r-1}} \leqslant \frac{q_r}{A^{\nu} q_r^{\nu}} = A^{-\nu} q_r^{\alpha}.$$

Hence from corollary (2), when $q_{r-1} \leqslant N < q_r$,

$$|S(\theta, N)| \leqslant \frac{1}{2}\left(\frac{N}{q_{r-1}} + a_{r-1} + a_{r-2} + \cdots + a_2\right)$$

$$\leqslant \frac{1}{2} A^{-\nu} (N^{\alpha} + q^{\alpha}{}_{r-1} + q^{\alpha}{}_{r-2} + \cdots + q_2^{\alpha})$$

$$\leqslant \frac{1}{2} A^{-\nu} (N^{\alpha} + q^{\alpha}{}_{r-1} + q^{\alpha}{}_{r-1} + q^{\alpha}{}_{r-1} \cdot 2^{-\alpha/2} + q^{\alpha}{}_{r-1} \cdot 2^{-2\alpha/2} + \cdots)$$

$$\leqslant \frac{1}{2} A^{-\nu} N^{\alpha} (3 + 2^{-\alpha/2} + 2^{-2\alpha/2} + \cdots)$$

$$= O(N^{\alpha}), \text{ when } \alpha > 0, \textit{ i.e.}, \text{ when } h > 2.$$

On the other hand when $h = 2$, $\alpha = 0$.

Then $S(\theta, N) = O(n)$.

But $q_{n-1} > 2 q_{n-3} > 2^2 q_{n-5} > \cdots > 2^{(n-2)/2}$.

So $n = O(\log q_{n-1}) = O(\log N)$.

Thus $S(\theta, N) = O(\log N)$.

THEOREM XIII: *When θ is an algebraic number of degree $r \geqslant 3$, $S(\theta, N) = O(N^{\alpha})$, where $\alpha = \frac{2\sqrt{r} - 2}{2\sqrt{r} - 1}$, and when θ is a quadratic number,*

$$S(\theta, N) = O(\log N).$$

From Siegel's theorem

$$\left|\theta - \frac{p}{q}\right| > \frac{A}{q^{2\sqrt{r}}} \text{ when } \theta \text{ is algebraic.}$$

Further when θ is quadratic, a_n is bounded so that $h = 2$.

Hence the theorem follows from the previous one.

Theorems XI, XII and XIII are also due to Hardy and Littlewood.

§ 7. *Results for Some More Special θ*

THEOREM XIV (Hardy): *When $\theta = \frac{\log a}{\log b}$ and is irrational, $S(\theta, N) = 0\left(\frac{N}{\log N}\right)$.*

Since $\log a_{n+1} = 0\,(q_n)$ in this case the result is immediate from corollary (2).

THEOREM XV (Hardy and Littlewood): *If ψ (n) is any function of* n *which steadily increases to infinity, there is a θ for which each of the inequalities* $S(\theta, N) > \frac{N}{\psi(N)}$ *and* $S(\theta, N) < -\frac{N}{\psi(N)}$, *is satisfied for an infinity of values of N.*

If $N = \left[\frac{a_n}{2}\right] q_{n-1}$ and $\psi(a_n) > 8\ q_{n-1}$ and $a_n \geqslant 2$, by putting $N_1 = 0$ in theorem IV, we get that $(-1)^{n-1} S(\theta, N) > \frac{1}{8} b_n = \frac{1}{8}(a_n - 1) \geqslant \frac{1}{16} a_n$

$$> \frac{1}{8} \cdot \frac{N}{q_{n-1}} \geqslant \frac{N}{\psi(a_n)} \geqslant \frac{N}{\psi(N)}.$$

So by choosing a_n so that $\psi(a_n) > 8\ q_{n-1}$ and by putting $N = \left[\frac{a_n}{2}\right] q_{n-1}$ we get the theorem.

THEOREM XVI: *Given $\delta > 0$, however small it may be, there exists a θ for which $S(\theta, N) > \delta$, for all N.*

In the continued fraction for θ,

let $a_{2r-1} = 1$ always and $a_{2n} \geqslant a_{2n-2} \geqslant \cdots \geqslant a_2 \geqslant 2$.

(a) $q_{2n} \leqslant N < q_{2n+1}$.

Then $h = 1$ as $a_{2n+1} = 1$.

Hence $1 - F_{2n+1} = 1 - \dfrac{1 + \dfrac{2N_1 + 1}{q_{2n}}}{1 + \dfrac{1}{x_{2n+2}} + \dfrac{q_{2n-1}}{q_{2n}}}$

$$\leqslant \frac{1}{x_{2n+2}} + \frac{q_{2n-1}}{q_{2n}} - \frac{2N_1 + 1}{q_{2n}} < \frac{1}{x_{2n+2}} + \frac{q_{2n-1}}{q_{2n}}$$

$$< \frac{1}{a_{2n+2}} + \frac{1}{a_{2n}}.$$

So from theorem I, for all N in $(q_{2n} \leqslant N < q_{2n+1})$,

$$S(\theta, N) - S(\theta, N_1) = \frac{(-1)^{2n} h}{2}(1 - F_{2n}) \leqslant \frac{1}{2}\left(\frac{1}{a_{2n}} + \frac{1}{a_{2n+2}}\right). \qquad (h)$$

(b) $q_{2n-1} \leqslant N < q_{2n}$.

(i) $h \leqslant a_{2n} - 1$.

Then $F_{2n} \leqslant \dfrac{a_{2n} - 1 + 2}{x_{2n} + t_{2n}} < \dfrac{a_{2n} + 1}{a_{2n} + 2 - \dfrac{1}{a_{2n+2}} - \dfrac{1}{a_{2n-2}}} \leqslant 1.$

$$\text{So } \frac{(-1)^{2n-1}h}{2}(1-F_{2n}) < 0.$$

(ii) $h = a_{2n}$.

Then $N_1 \leqslant q_{2n-2} - 1$, and so $2N_1 + 1 < 2q_{2n-2} - 1$.

So,

$$(x_{2n} + t_{2n})(1 - F_{2n}) = \frac{1}{x_{2n+1}} - \frac{2N_1 + 1 - q_{2n-2}}{q_{2n-1}}$$

$$> \frac{1}{x_{2n+1}} - \frac{1}{q_{2n-1}} > 0.$$

Under the conditions imposed on a_r, it is easy to verify the last inequality; to avoid printing difficulty, I omit the proof. Hence, in this case also

$$\frac{(-1)^{2n-1}h}{2}(1-F_{2n}) < 0.$$

Therefore, from theorem I,

when $q_{2n-1} \leqslant N < q_{2n}$,

$$S(\theta, N) - S(\theta, N_1) < 0. \qquad (i)$$

By applying the inequalities (*h*) and (*i*) successively, we get that, when $q_{n-1} \leqslant N < q_n$,

$$S(\theta, N) \leqslant \frac{1}{a_2} + \frac{1}{a_4} + \cdots + \frac{1}{a_{2s}}, \text{ where } 2s \leqslant n+2, \text{ and so}$$

$$S(\theta, N) \leqslant \sum_{r=1}^{\infty} \frac{1}{a_{2r}}.$$

But given δ, we can choose a_{2r} so that

$$\Sigma \frac{1}{a_{2r}} < \delta, \text{ and } a_{2r} \geqslant a_{2r-2} \geqslant \cdots \geqslant a_2 \geqslant 2.$$

The theorem follows immediately from this.

Similarly we can prove

THEOREM XVII. *Given* $\delta > 0$, *we can find* a θ *for which*

$$S(\theta, N) > -\delta \text{ for all } N.$$

Theorems XVI and XVII are interesting when they are compared with theorems V and VIII.

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APPLICATION OF TENSOR ANALYSIS TO MOLECULAR ANISOTROPY

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1. Introduction

Recently[1] attempts have been made to calculate the mean polarisability and anisotropy of a molecule in terms of the principal polarisabilities of its constituent bonds. The basic assumption in these attempts is to ascribe polarisabilities to the individual bonds and neglect the interactions between the bond polarisabilities. As a consequence of this assumption it would follow that the polarisability tensor of a molecule can be obtained by a tensorial addition of the polarisability tensors of the individual bonds. The invariants connected with the molecular tensor (*i.e.*) the mean polarisability and the anisotropy of the molecule can then be evaluated in terms of the invariants of the bond tensors. The same type of problem occurs in the evaluation of the magnetic anisotropy of a molecule in terms of its bond anisotropies, or the magnetic anisotropy of a crystal in terms of its molecular anisotropies. Putting it generally, the problem consists in considering the tensor ellipsoid of a system compounded of a number of tensor ellipsoids, which may be oriented in any arbitrary manner, and expressing the invariants of the system in terms of the invariants of the constituent ellipsoids of the system. It is well known that the spur or sum of the diagonal terms of a tensor is an invariant. It is further, a linear function of the tensor components and hence it follows from the basic assumption of the additivity of bond tensors that the spur of the individual ellipsoids can be directly added up to give the spur of the entire system. The spur of the system is thus independent of the orientations of its constituent ellipsoids. The sum of the squares of all the tensor components is another well-known invariant connected with a tensor. But it does not permit us to derive the quadratic invariant of the system by a simple addition of the quadratic invariants of its constituent tensors, since the basic assumption postulates only a linear addition of the tensor components. We must utilize the basic assumption to derive, at first, the tensor of the entire system

and then compute the quadratic invariant of this tensor. It is evident that the tensor of the entire system of tensor ellipsoids obtained by a tensorial addition of the individual ellipsoids, will necessarily be a function of their orientations and hence its quadratic invariant will depend upon their mutual orientations. It is proposed to derive below an expression for this invariant.

We consider a system of 'n' tensor ellipsoids oriented in an arbitrary manner. The principal axis of the 'r'th ellipsoid will be denoted by $K_\mu^{(r)}$ ($\mu = 1, 2, 3$) and their direction cosines with respect to a fixed frame of reference (OXYZ) by $l_{\mu\nu}^{(r)}$ ($x = x, y,$ or z). The tensor component $\alpha_{xy}^{(r)}$ of this tensor, in the fixed frame of reference is given by

$$\alpha_{xy}^{(r)} = \sum_{\mu=1}^{3} K_\mu^{(r)} l_{\mu x}^{(r)} l_{\mu y}^{(r)}. \tag{1}$$

This can be easily derived from simple tensor transformation laws.
Hence α_{xy}, the tensor component for the whole system, consisting of 'n' individual tensors, is given by

$$\alpha_{xy} = \sum_{r=1}^{n} \alpha_{xy}^{(r)} = \sum_{r=1}^{n} \sum_{\mu=1}^{3} K_\mu^{(r)} l_{\mu x}^{(r)} l_{\mu y}^{(r)}. \tag{2}$$

Squaring each tensor component and adding, we have,

$$I = \sum_{x,y} \left| \alpha_{xy} \right|^2 = \sum_{x,y} \sum_{\mu,\nu} \sum_{r,s} K_\mu^{(r)} K_\nu^{(s)} l_{\mu x}^{(r)} l_{\mu x}^{(s)} l_{\mu y}^{(r)} l_{\mu y}^{(s)}$$

$$= \sum_{r,s} \sum_{\mu,\nu} K_\mu^{(r)} K_\nu^{(s)} \cos^2 \theta_{\mu\nu}^{(rs)} \tag{3}$$

where $\theta_{\mu\nu}^{(rs)}$ is the angle between $K_\mu^{(r)}$ and $K_\nu^{(s)}$.

2. *Application to the Optical Anisotropy of a Molecule*

If α_{xy} be the polarisability tensor of a molecule, it can be split up into "isotropic" part σ_{xy} and "anisotropic" part γ_{xy} as

$$\alpha_{xy} = \sigma_{xy} + \gamma_{xy} \tag{4}$$

$$\sigma_{xy} = \sigma \cdot \delta_{xy} \text{ with } \sigma = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\delta_{xy} = 0 \text{ if } x \neq y$$

$$= 1 \text{ if } x = y$$

and

$$\gamma_{xy} = \alpha_{xy} - \sigma_{xy}. \tag{5}$$

σ_{xy} is a diagonal tensor whose diagonal terms are equal, and which transforms into itself. Hence γ_{xy} is also a tensor and is referred to in the following as the anisotropic tensor. The sum of its diagonals is zero. In the principal frame of a molecule, with principal polarisabilities A, B and C

the isotropic and anisotropic tensors are

$$\begin{pmatrix} \frac{A+B+C}{3} & 0 & 0 \\ 0 & \frac{A+B+C}{3} & 0 \\ 0 & 0 & \frac{A+B+C}{3} \end{pmatrix}; \begin{pmatrix} \frac{2A-B-C}{3} & 0 & 0 \\ 0 & \frac{2B-C-A}{3} & 0 \\ 0 & 0 & \frac{2C-A-B}{3} \end{pmatrix} \quad (6)$$

The anisotropy of the molecule γ, or rather its square γ^2 is defined as[2]

$$\gamma^2 = \frac{3}{2} \sum_{x,y} \gamma_{xy}^2. \quad (7)$$

In the principal frame of the molecule, it reduces to the usual form

$$\gamma^2 = A^2 + B^2 + C^2 - AB - BC - CA. \quad (8)$$

When two of the principal axes, say B and C, are equal, say as in the case of a bond, the above expression reduces to the form

$$\gamma^2 = (A - B)^2. \quad (9)$$

We define $\gamma = A - B$ choosing the positive square root in (9). This means that the anisotropy γ is defined only if two of the three principal polarisabilities are equal. According to our definition the anisotropy γ could be + ve or − ve depending on $A \gtrless B$.

Thus the anisotropy of the 'r'th bond, $\gamma^{(r)}$ is given by

$$\gamma^{(r)} = A^{(r)} - B^{(r)} \quad (9)$$

Here $A^{(r)}$ is the principal polarisability which is not equal to either of the other two; it is the polarisability along the length of the bond, while $B^{(r)}$ is the polarisability in two perpendicular directions.

We can directly apply the formula to find the molecular anisotropy in terms of bond anisotropies. The molecule will be assumed to be made up of 'n' bonds, the bonds being not necessarily chemical bonds. The interactions between atoms unconnected by chemical bonds, may be taken into account by postulating as if there were "bonds" between such atoms. The general validity of formula (3) permits us to include in it this type of interaction also.

Applying (7) and (3) we have

$$\gamma^2 = \frac{3}{2} \sum_{x,y} \gamma_{xy}^2 = \frac{3}{2} \sum_{x,y} \sum_{r,s} \gamma_{xy}^{(r)} \gamma_{xy}^{(s)} = \frac{3}{2} \sum_{\mu,\nu} \sum_{r,s} K_{\mu}^{(r)} K_{\nu}^{(s)} \cos^2 \theta_{\mu\nu}^{(rs)}. \quad (10)$$

Here K_{μ}^{r}, ($\mu = 1, 2, 3$), are the principal values of the anisotropic tensor of

the 'r'th bond. This tensor is represented by

$$\begin{pmatrix} \frac{2}{3}(A^{(r)}-B^{(r)}) & 0 & 0 \\ 0 & -\frac{1}{3}(A^{(r)}-B^{(r)}) & 0 \\ 0 & 0 & -\frac{1}{3}(A^{(r)}-B^{(r)}) \end{pmatrix} \tag{11}$$

so that

$$\left.\begin{aligned} K_1^{(r)} &= \frac{2}{3}\gamma^{(r)} \\ K_2^{(r)} = K_3^{(r)} &= -\frac{1}{3}\gamma^{(r)} \end{aligned}\right\} \tag{12}$$

Substituting these values in (10) we find

$$\gamma^2 = \frac{1}{2}\sum_{r=1}^{n}\sum_{s=1}^{n}\gamma^{(r)}\gamma^{(s)}(3\cos^2\theta^{(rs)}-1) \tag{13}$$

where $\theta^{(rs)}$ is the angle between the rth and sth bonds.

This formula is of a general nature and can be applied to molecules whose principal frame is not easy to determine. It can be verified to vanish for tetrahedral molecules CCl_4, CH_4 etc. When applied to molecules $CHCl_3$ and CH_3Cl, it yields the result that both have the same numerical value of the optical anisotropy (taking only the chemical bonds into consideration). The anisotropy of CH_2Cl_2 turns out to be $\frac{2}{\sqrt{3}}$ times the anisotropy of $CHCl_3$ or CH_3Cl.

When two of the three principal polarisabilities of the molecule are equal, the anisotropy itself can be defined, as observed earlier. If in addition, the principal frame of the molecule can be determined by inspection, the expression for the anisotropy can be given in a simpler form. If a_{xx}, a_{yy}, a_{zz} are the diagonal components of the molecular tensor in the principal frame and if $a_{yy}=a_{zz}$, the anisotropy is given, from (9) by

$$\gamma = a_{xx}-a_{yy} = \sum_{r=1}^{n}\left(a_{xx}^{(r)}-a_{yy}^{(r)}\right)$$

$$= \frac{1}{2}\sum_r \gamma_r\left(3l_r^2-1\right), \tag{14}$$

where l_r is the cosine of the angle between the 'r'th bond and the principal axis of the molecule which is not equal to the other two. The formula (14) can be applied to determine the static or Rayleigh anisotropies of molecules with axial symmetry. It is evident however, that it cannot be, in general, applied to determine the variation in the optical anisotropy of a molecule caused by a

variation in the bond anisotropies, as in the case of Raman scattering; for, the axial symmetry of the molecule may not be retained during any specific vibration, and so one has to use the formula (13) rather than (14) in such cases. The application of the formulæ to specific cases will be dealt with in another paper.

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Summary

By employing the invariant definition of the anisotropy of a molecule, a general expression for the same is derived in terms of the anisotropies of its individual bonds.

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